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OFFSHORE PRODUCT QUALITY

FINAL PROJECT REPORT

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MICROMEDIA

EXECUTIVE SUMMARY

The purpose of this project was to contribute to the improvement of potash products exported to offshore customers by Saskatchewan potash producers. Co-operation among member companies of Canpotex, the potash marketing agency, has resulted in the development of three laboratory test methods for determination of the durability, dedusting and anticaking characteristics of potash products. Because Canpotex markets similar products from ten different production centres in Saskatchewan, the adoption of standard test procedures for product analysis is essential to guarantee product quality for offshore customers.

The Degradation Test has been evaluated in a round-robin campaign by all participating companies. A procedure and equipment is recommended which will facilitate the measurement and comparison of the durability of Granular and Coarse grades of potash. Controlled ball milling and screen analysis of a narrow size range of sample (-8+10 mesh material) is used to determine the resistance of potash to impact and abrasion under reproducible conditions. Trials have shown that data from different laboratories are acceptable for product comparisons and internal quality control applications.

The Dedusting Test developed by the Potash Corporation of Saskatchewan (PCS) is shown to yield highly reproducible results with low standard deviation on data. The performance of dust-scavenging additives such as hydrocarbon oils can be determined with confidence. In addition, time-dependent dedusting properties of reagent-treated products have been observed. Data collected using this dedusting test method should contribute better understanding of "shelf-life" limitations of potash products.

The Anticaking Test was refined during the term of this project and a preliminary laboratory procedure is described. Control of the moisture, temperature and handling and compaction history of potash samples has improved the reproducibility of failure loads required to fracture intentionally caked material. This test improvement has provided a capability to evaluate the performance of chemical additives which are used by potash producers to condition the surface of products so as to minimize the tendency to cake or

set up in storage. Examples are provided in the report of the behaviour of a Granular grade of potash treated with different anticaking agents.

The scientific basis for Offshore Product Quality is explored in a concluding section of this report so as to focus attention on the fundamental physical and chemical properties of potash materials. Traditionally, the fertilizer industry has relied upon the results of inadequate empirical tests, and field observations and experience, to improve the quality of potash materials delivered to offshore customers. Correct interpretation of product quality studies in terms of the science of potash materials will ensure that future developments contribute to progress.

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L'objectif principal de ce projet était de concourir à l'accroissement de la qualité des produits potassiques de Saskatchewan destinés à l'exportation outremer. La coopération des compagnies actionnaires de Canpotex, qui est l'agent de commercialisation à l'étranger, a permis le développement de 3 tests de laboratoire pour déterminer la durabilité des produits potassiques, les propriétés d'abattement de la poussière et d'anti-consolidation de certains agents chimiques. Pour Canpotex, qui met en marche des produits similaires provenant de 10 sources différentes, l'adoption de tests étalons est essentielle pour garantir une qualité uniforme.

Le test de détérioration (durabilité) a été évalué conjointement par toutes les compagnies participant au projet. Pour déterminer la résistance à l'impact et à l'abrasion, les produits potassiques sont soumis à un broyage contrôlé. Par la suite, une analyse de changement de granulométrie est utilisée pour déterminer un indice de détérioration. Les essais ont démontré que les résultats obtenus par différents laboratoires sont compatibles pour fins de comparaison et de contrôle de qualité interne. Une description du test, ainsi que l'équipement nécessaire sont recommandés.

Le test de dépoussièrage développé par Potash Corporation of Saskatchewan (PCS) s'est avéré très fiable et reproductible en générant des résultats avec de faibles déviations standards. L'efficacité des réactifs de dépoussièrage, telque les huiles hydrocarbures, peut être évaluée avec confiance. Aussi, le rendement de ces réactifs en relation du temps a pu être étudié. Les résultats obtenus devrait permettre une meilleur compréhension des temps limites d'entrepasage des produits de potasse.

Le test anti-consolidation a été amélioré durant la durée de ce projet, et une description préliminaire du test étalon est présenté dans ce rapport. Le contrôle de l'humidité, de la température, des conditions de manutention, et de compaction a permis d'améliorer le reproductibilité des charges nécessaire pour fracturer les échantillons consolidés intentionnellement. L'amélioration du test a permis d'évaluer les performances des agents chimiques qui sont

utilisés pour le conditionnement de la potasse afin de minimiser la consolidation et l'agglomération durant les périodes d'entreposage. Des examples décrivant le comportement de produits "Granuleux" traités avec différents réactifs sont inclus dans ce rapport.

Le fondement scientifique du projet, tel que les propriétés physiques et chimiques fondamentales de la potasse, est discuté dans la dernière partie du rapport. Traditionnellement, l'industrie de l'engrais se fiait sur des résultats provenant de tests empiriques, sur l'observation et l'expérience personnelle, pour améliorer la qualité de produits potassiques destinés outremer. L'interprétation rigoureuse d'études de qualité des produits potassiques contribuera à l'avancement de nouveaux développements.

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INTRODUCTION

Purpose of the Offshore Product Quality Project

This study was designed to improve the quality of Saskatchewan potash products delivered to fertilizer customers in offshore markets.

The project was assigned high priority by member companies of the Saskatchewan Potash Producers Association and included in the set of joint venture research and development initiatives that was proposed for co-funding under the Canada/Saskatchewan Mineral Development Agreement. To ensure that the project would have a direct impact on international marketing activities, provision was made for close co-operation with the Technical Committee of Canpotex, the producer-owned potash marketing agency.

Importance of Offshore Potash Markets

During the five year period 1982 to 1986 Canpotex sold 16.3 million tonnes of potash products to client nations outside North America. About 32% of the Saskatchewan potash production of 51.2 million tonnes during this period was shipped to export market customers. The cumulative value of these offshore potash commodity sales was over $1 billion.

Concern for Quality of Potash Products

As Saskatchewan is the leading potash exporter in the Western world, continuation of traditional Canpotex product standards was recognized to be important to retain existing and to expand future markets.

Two factors provided the motivation for commitment to this project. First, industry competitors in the USSR, German Democratic Republic, Israel and Jordan had improved their capability to deliver better product to the marketplace. Second, the trend towards coarser grades of potash, away from standard grade material, had stressed the importance of maintaining specifications and integrity of products under increased stresses imposed by product handling and environmental exposure conditions.

Potash products are granular mixtures of potassium chloride which may include natural crystals, processed crystals, or agglomerates prepared by compaction of finer material, that meet the size distributions or grades required by customers (1). Each type of particle responds uniquely to abrasion, impact, or change in atmospheric humidity that may occur between the potash mine site and the end user of the product.

Each potash producer has endeavoured independently to deliver uniform, durable, free-flowing, dust-free products to its customers. Because approaches to achieving this product quality goal differed among member companies of Canpotex, and because the materials handling practices of Canpotex frequently required co-mingling of similar potash products from two or more mine sites, the need was recognized to focus project attention specifically on the quality of Saskatchewan potash product shipped to offshore destinations.

Offshore Product Quality

Potash product specifications issued to customers by Canpotex (see Appendix I) show the importance of chemical composition and particle size distribution of these granular materials. Minimum potassium (K) content, generally expressed as K_2O equivalent or KCl weight percent, is guaranteed to ensure that customers receive their expected fertilizer nutrient input for agricultural use. Analytical methods to measure, and process operating techniques to control, the composition of potash products are well developed. Delivery of potash which meets composition specifications generally does not pose a problem for Saskatchewan producers.

Grades of fertilizer potash are differentiated by the particle size distribution characteristics specified in Canpotex data sheets. Offshore demand for Granular, Coarse, Standard, and other Canpotex products is summarized in Table 1.

TABLE 1. CANPOTEX OFFSHORE POTASH SALES BY GRADE, 1982-1986

Product Grade		1982	1983	1984	1985	1986
Granular	kt	321	422	562	492	531
	%	13.7	12.8	13.5	16.7	15.0
Coarse	kt	184	279	271	165	306
	%	7.9	9.0	6.5	5.6	8.6
Standard	kt	1466	2151	2774	1730	2043
	%	62.5	65.3	66.6	58.8	57.8
Special Standard	kt	203	224	309	250	351
	%	8.7	6.8	7.4	8.5	9.9
Soluble*	kt	168	197.7	246	299	301
	%	7.1	6.0	5.9	10.2	8.5
Chemical	kt	1.5	1.8	1.8	1.8	2.3
	%	0.06	0.05	0.04	0.06	0.06
Total	kt	2343	3293	4163	2939	3534

* Includes both 0.5% and 1.0% NaCl products

Customer selection of grades for agricultural use depends in part upon application methods and technology used by farmers in each country. If Saskatchewan potash is blended with other granular nitrogen or phosphate products, it is necessary that particle size distributions be similar so as to minimize segregation of components in nutrient mixtures. The trend towards bulk blending of N, P and K fertilizers in offshore markets, as has already occurred in North America, has required Canpotex member companies to co-operate on delivery of products with more tightly specified size distributions so as to ensure compatibility with other N and P nutrients.

Two other potash product characteristics, not included in the summary of specifications, also contribute importantly to customer perceptions of quality:

* Durability. The capability of a friable potash material to withstand mechanical stress during storage, transport and handling operations is

readily apparent to customers. The observation of an excessive amount of fines in sampled material, or of potash dust entrained in air during handling, may be used to diagnose poor product quality. The industry has traditionally used dedusting additives to control dispersion of fines.

* Flowability. Customers expect potash products to remain as free-flowing granular materials. However, because potash, like other N and P fertilizers, is hygroscopic it can readily exchange moisture with air. This can induce interparticle caking by recrystallization of soluble potash at particle contacts. The adverse consequence of this dynamic process is product caking which can create severe handling problems for shippers or customers. Anticaking surface treatments are used to reduce the potential for product set-up or cementing before field application of the fertilizer.

Standard Test Methods for Evaluation of Product Quality

The measurement of potash composition and particle size distribution is a routine practice in control laboratories of potash producers to ensure that Canpotex product specifications are met. These procedures are discussed more fully later in this report.

However, in spite of decades of study by fertilizer development agencies (2,3), at the outset of this project universally recognised test methods did not exist by which to measure potash product resistance to mechanical degradation, dust generation or caking. As the prediction of product performance under probable exposure conditions in offshore market environments would greatly benefit both international marketing initiatives and product development, this project set out to correct this shortcoming in product test methods.

DETERMINATION OF THE SCOPE OF THE OFFSHORE PRODUCT QUALITY PROJECT

Role of the Saskatchewan Potash Producers Association (SPPA)

All Saskatchewan potash producers are members of the boards and committees of both the SPPA and Canpotex. The present project was planned so as to support the offshore product quality requirements of Canpotex, and the SPPA Research and Development Committee selected the present topic for attention after consultation on the allocation of co-funding from the Canada/Saskatchewan Mineral Development Agreement.

The original project description and budget prepared for the SPPA was also reviewed by the Canpotex Technical Committee and the scope was agreed to, subject to detailed review by project participants from each company. This proposal provided the basis for response by the lead company, the Potash Corporation of Saskatchewan, to the request issued by Supply and Services Canada that activated this project.

A copy of the original SPPA proposal is attached as Appendix II.

Review of Industry Requirements and Consultation on Project Scope

Eighteen industry experts on quality control of potash products met in Saskatoon on November 25, 1986 to review the scope of the SPPA proposal, to set priorities for laboratory studies, and to allocate project funding for the work. The full summary of this meeting is attached as Appendix III.

Laboratory analyses for K_2O grade, size distribution, moisture content, resistance to degradation or dust generation, levels of anticaking amine and dedusting oil, and caking tendency were described by each company representative. The results of this review are presented in Table 2. The listing confirms that there is general consistency among methods used for chemical or reagent composition measurements, product moisture determinations, and screen size analyses. These laboratory tests enable compliance with published Canpotex product specifications in a consistent manner.

Inspection of the Table 2 test procedures for degradation, dusting and caking of potash products also highlights the lack of recognized standard methods for determination of these properties. Availability of reliable, reproducible laboratory tests that yield results which can be correlated with the performance of products through the offshore storage and distribution system would greatly facilitate the control of quality at the production stage.

Three requirements were identified at this participants' meeting that defined priorities for this project. These were:

(1) Evaluation of the product degradation test developed by Wist of PCS Mining, by fabrication and delivery of standard test equipment to each company, scheduling of a round-robin test program using reference potash products from different mine sites, and assessment of laboratory results. The objective of this task was to create a standard product degradation test for use by Canpotex member companies.

(2) Investigation of instrumentation and development of methods for monitoring of potash product in the field. Changes in moisture content of material contained in storage facilities, railcars, shipholds and free standing piles is considered to affect product durability and the potential for massive caking. The objective of this task was to deliver technical recommendations on test methods for field monitoring of moisture content, relative humidity and temperature.

TABLE 2. PRODUCT QUALITY LABORATORY ANALYSES OF SASKATCHEWAN POTASH PRODUCERS

Potash Producer	K_2O Grade	Size Distribution	Moisture	Degradation Test	Dusting	Amine	Oils	Caking Test
CCP	XRF	Screen Analysis SGN Calc.	Weight Loss, 105°C	Rotating Drum	Air Entrainment Test	Extraction Titration		Humidity Chamber
Cominco	XRF Calibrated by STPB	Screen Analysis SGN Calc.	Coulometry, Karl Fischer	Ro-Tap Test Method	None	Soxhlet Extraction Gravimetric Colorimetric		Working on R.H. Cabinet Test
IMC	XRF Flame Photometer	Screen Analysis	Gravimetric	Milling Test	-	Colorimetric	Gravimetric	None: Field Observation
Kalium		Manual Screen Analysis	Gravimetric Heat to m.p. for total	Method #7 (See paper) Impact Test	Air Entrainment Test			R.H. Chamber cf. TVA
PCA	Flame Photometry		Gravimetric	Rotating Drum type		Colorimetric		
PCS Mining: Allan Division	Red Prod: STPB White Prod: Flame Photometry	Tyler Screen Analysis Rotap	Gravimetric 105°C	Wist Drum Test	Entrainment Test	Titration Colorimetric Picric Acid	Extraction Gravimetric	Pellet Breakage
Cory Division	Flame Photometry	Screen Analysis, Rotap	Gravimetric 110°C	Wist Drum Test	Entrainment in Air Flow	Extraction, Colorimetric	Extraction, Gravimetric	Humidify, Heat, Pellet Breakage
Lanigan Division	XRF	Screen Analysis SGN Calc.	Gravimetric 3h, 110°C	Wist Drum Test	Entrainment Test	Colorimetric or NaLS	Extraction, Gravimetric or U.V. Absorption (Spectrophotometer)	No Routine
Rocanville Division	XRF	Screen Analysis	Gravimetric 1h, 105°C	Wist Drum Test	None	Colorimetric		TVA Type Test

Abbreviations: XRF : X-ray Fluorescence
STPB: Sodium tetraphenyl boron, an analytical reagent
R.H.: Relative Humidity

(3) Assessment of the effectiveness of additives used to modify the surface properties of potash materials so as to reduce the risk of caking in storage. The specific task objective was to recommend laboratory test conditions that would facilitate a reliable, reproducible comparison of anticaking performance of additives, based on both the existing experience of participating companies and theoretical factors.

The project priorities selected by member companies were reported to the Technical Committee of Canpotex for similar consideration as part of the provision for liaison with this advisory group which supports the needs of the potash export agency.

TECHNICAL DISCUSSION

TASK ONE: DEVELOPMENT AND EVALUATION OF A PRODUCT DEGRADATION TEST FOR CANPOTEX PRODUCTS.

Background

As noted in the previous section of this report, the durability of Saskatchewan potash products must be sufficiently high so as to withstand handling and environmental stress between the plant gate and the offshore customer. Each Canpotex member company used a different quality control laboratory method to test durability of product. Project participants agreed that the method developed and used by the divisions of PCS Mining would be adopted as the basis for the project initiative.

The PCS Mining test was itself a modification of a ball mill procedure recommended (2) by the Fertilizer Development Centre of the Tennessee Valley Authority (TVA). Selection of parameters and ranges for study in the round-robin test phase of this work was based on the experience of PCS Mining.

Equipment Design, Fabrication and Commissioning

Eleven identical ball mill units were built by PCS Mining personnel according to the design illustrated in Figure 1. The ball mill chamber was a right cylinder of internal diameter 190 mm and width 64 mm, with six 12 mm flights equally spaced around the inner circumference. The removable front cover had a central stoppered 50 mm diameter opening for charging material.

Each unit was delivered with two electric motors* with a shaft rotational specification of 30 rpm under full load. Commissioning trials indicated that actual values were constant to within 1 percent of the average of 33.4 rpm. No attempt was made to alter this rate.

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* Electric Motors supplied by: Dayton Electric Manufacturing Co., Chicago, U.S.A. 60648. Model #3M329, 1/15 HP, 30 rpm (full load), 120 V, TEFC Shaded Pole, 125 inch-pounds.

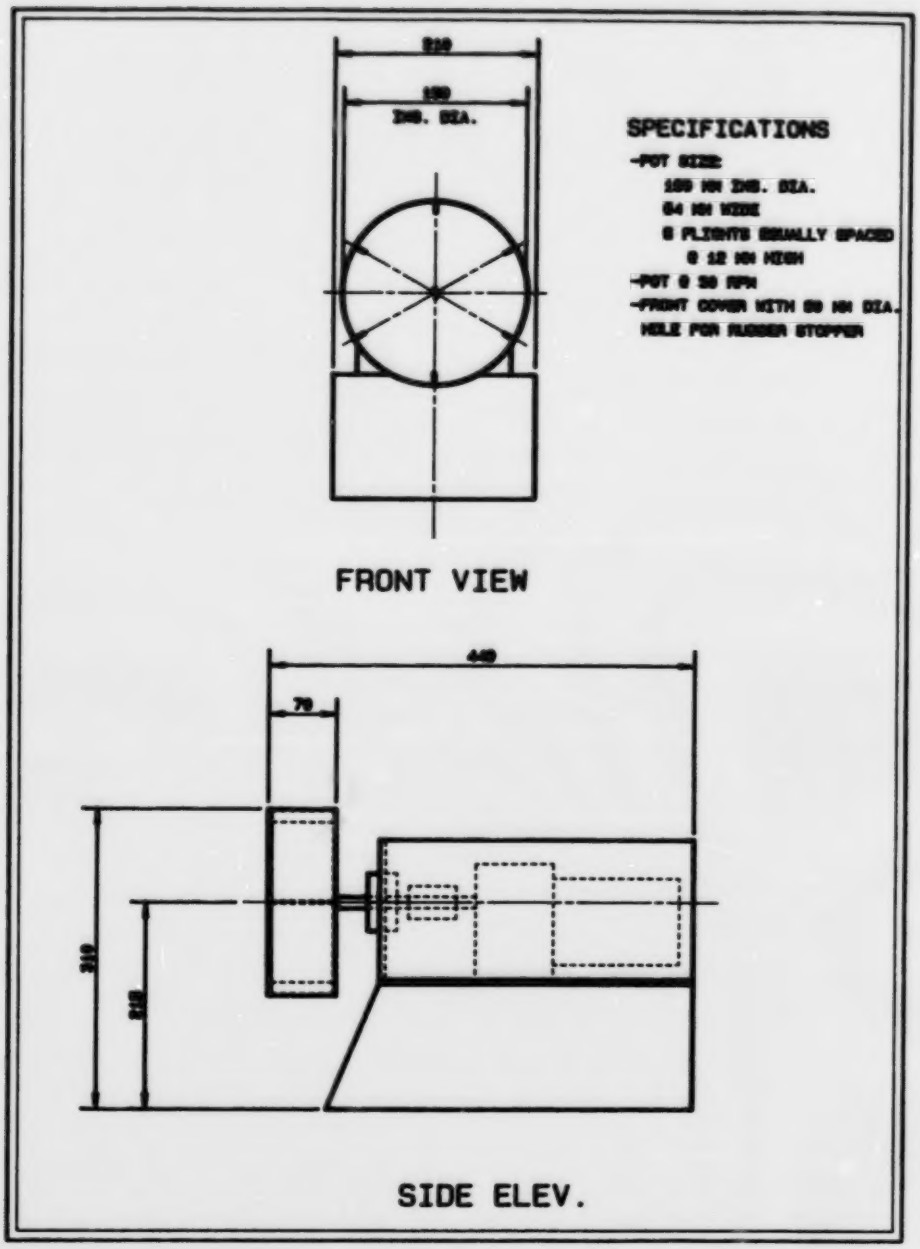

Figure 1. Design of the Standard Ball Mill for Potash Degradation Test

The results of preliminary product degradation trials are summarized in Table 3. Using compacted product from the Lanigan Division of PCS Mining with a Size Guide Number (SGN) of 210, a mean degradation index of 8.40 ± 0.29 (one standard deviation) was measured over all runs. Refer to the procedure below for an explanation of the basis of this index value.

Reference Materials for Round Robin Test

Three types of product were selected as reference materials for use by each participant in evaluation of the test procedure and equipment. Two kilograms of potash product were delivered by the contributing site to each laboratory, as follows:

- IMC Coarse, a natural crystal product recovered by heavy media separation of Esterhazy member ore and sized by screening;

- Kalium Chemicals Granular, a white material produced by compaction and screening of potash separated by crystallization from solution mine brines;

- PCS Mining Cory Division Granular, a red product recovered by flotation and finished by compaction and screening.

TABLE 3. Commissioning Trials of Ball Mill Equipment Used for Product Degradation Test Assessment

Unit No.	Receiving Minesite	Experiment Number 1	2	3	4	Average	Standard Deviation
1	IMCC, K1	8.1	8.5	8.6	8.7	8.5	0.23
2	IMCC, K2	8.8	8.9	8.5	8.0	8.6	0.35
3	Cominco	8.1	8.4	8.5	8.6	8.4	0.19
4	PCS Cory	7.8	8.1	8.3	8.3	8.1	0.20
5	PCS Lanigan	8.2	8.4	8.5	8.5	8.4	0.12
6	Kalium	8.0	8.1	8.1	8.5	8.2	0.19
7	PCS Allan	8.9	9.0	8.3	9.0	8.8	0.29
8	PCS Rocanville	8.8	8.6	9.0	8.3	8.7	0.26
9	Central Canada Potash	8.3	8.6	8.6	8.5	8.5	0.12
10	PCS R&D	8.3	8.6	8.3	8.4	8.4	0.12
11	PCS R&D	8.1	8.2	8.5	8.4	8.3	0.16
	Average					8.4	0.20

Reference Laboratory Procedure and Test Results

Participants were requested to measure the degradation index of each of the three materials described above, according to the following reference procedure:

- Charge one hundred grams of plus 10 mesh (Tyler screen) product as received into the mill chamber.
- Add 25 x 0.5 inch diameter steel balls to the mill chamber.
- Rotate the chamber for 5.00 minutes at 33 rpm.
- Screen all ball mill product for 2.0 minutes on a 20-mesh screen assembly installed in a Rotap shaker with the hammer down.

- Report the degradation index as the weight percent of material which passes through the 20-mesh screen.

Results are summarized in Table 4 for each reference product tested by all participating laboratories. Note that the Potash Company of America (PCA) was unable to contribute to this work because of mine flood control priorities. The PCS Mining R&D group completed this test assignment for PCA.

The data confirm that the test equipment and reference procedure and materials yielded reproducible results in ten different laboratories. Results were consistent within the subsets of product types and differences among averages were significant enough to distinguish among product types. Note that the large average value for IMC coarse product of 20.1 percent is characteristic of this type of material in impact- or ball mill-type laboratory tests, and appears to overestimate actual degradation of reagent-treated natural crystal product observed in the field.

TABLE 4. Summary of Degradation Index Measurements on Reference Products by Participating Laboratories in the Round Robin Trials

Minesite	IMC Coarse 1	2	3	4	Ave.	Kalium Granular 1	2	3	4	Ave.
IMC K1	21.9	22.1	23.3	23.4	22.7	6.0	6.7	6.5		6.4
IMC K2	20.3	21.8	21.1	20.9	21.2	5.9	6.1	6.5		6.2
				22.1						
Cominco	18.7	18.8	18.8		18.8	6.4	6.5	6.5		6.5
Cory	19.7	20.0	19.9		19.9	6.0	6.0	5.9		6.0
Lanigan	19.6	18.6	18.9		19.0	6.0	6.0	6.3		6.1
Kalium	Average of 4				20.4	Average of 10				7.0
Allan	19.4	19.6	19.8		19.6	5.9	5.5	6.1		5.8
Rocanville	18.3	18.9	18.7	18.8	18.7	6.1	5.7	6.5	5.6	6.0
C.C.P.	19.4	19.5	19.8		19.6	5.3	5.5	5.7		5.5
PCS R&D	20.8	19.6	20.4		20.3	5.7	5.9	5.7		5.8
PCS R&D	21.3	20.6	19.4		20.4	6.0	6.0	5.8		5.9
Average					20.1					6.1
Standard Deviation					1.11					.39
Range				18.7 to 22.7					5.5 to 7.0	

Minesite	Cory Granular 1	2	3	Ave.
IMC K1	9.1			9.1
IMC K2	8.6	8.4	8.5	8.5
Cominco	7.9	8.0		8.0
Cory	7.4	7.4	7.4	7.4
Lanigan	7.3	7.3	7.7	7.4
Kalium	Average of 4			8.0
Allan	7.6	7.6	7.9	7.7
Rocanville	6.9	7.4	7.3	7.2
C.C.P.				
PCS R&D	7.7	7.2	7.6	7.5
PCS R&D	7.6	7.9	8.0	7.8
Average				7.9
Standard Deviation				.55
Range			7.2 to 9.1	

Effect of Variables on Degradation Test Results

Participants were assigned additional tasks to investigate the effect of test feedstock particle size distribution, number and size of steel balls charged to the mill, and time of milling. The results of these runs are summarized in Tables 5 to 7. Granular product from the PCS Mining Cory Division was used as the reference material by all laboratories.

The size distribution of crushed product from these sets of ball mill runs was determined by sieving through a set of screens from 6 to 100 mesh as listed in the left hand column of each table. Knowledge of the detailed size distribution was necessary to further refine the final experimental procedure that would form the basis of the recommended standard test. Conditions that would yield a typical Degradation Index for control purposes of about 5 to 10 weight percent were sought.

As expected, an increase in mesh size of the feed, time of milling, and number or size of the steel balls all contributed to increased Degradation Index determined as the weight percent of potash passing through the 20 mesh screen.

The full set of data was reviewed by a panel of control laboratory experts and the detailed requirements of the reference test procedure were modified based on the experience of this round robin test. A report on the discussion of standard test conditions is included below.

The direct cost of this round robin test assessment to industry participants was $20,155.78. This represents most of the potash industry $25,000 commitment to the project.

Standard Procedure: Canpotex Ball Mill Test

After review of the results from the round-robin analyses described above, and detailed consideration of the consequences of each step of the proposed test protocol, a final procedure was drafted and adopted by participants. The test method reprinted on page 19 is the principal technical contribution made by this project.

TABLE 5. Effect of Feedstock Size Range and Time of Milling on the Final Product Particle Size Distribution (25 x 0.5 Inch Diameter Steel Balls; Cory Division Granular Product)

Table 5a

Mesh	2 Minutes -6+8	-8+10	-10+14	All+14
- 6	100.0			98.8
- 8	14.4	100.0		67.6
- 10	5.6	17.1		27.1
- 14	2.7	6.0	12.5	6.5
- 20	1.9	3.6	5.7	3.8
- 28	1.3	2.3	3.1	1.8
- 35	1.0	1.6	1.9	1.4
- 48	0.7	1.2	1.3	0.8
- 65	0.6	0.8	0.9	0.5
-100	0.5	0.6	0.5	0.3

Table 5b

5 Minutes -6+8	-8+10	-10+14	All+14
100.0			99.1
30.1	100.0		73.9
13.9	34.5	100.0	38.4
7.7	15.8	29.6	16.2
5.6	10.0	14.7	9.8
4.1	6.6	8.4	6.0
3.2	4.7	5.5	4.7
2.5	3.5	3.7	3.0
2.0	2.6	2.5	2.1
1.6	1.9	1.7	1.5

Table 5c

Mesh	10 Minutes -6+8	-8+10	-10+14	All+14
- 6	100.0			99.4
- 8	52.6	100.0		82.5
- 10	30.2	57.9		55.3
- 14	18.7	32.6	51.7	32.1
- 20	14.1	22.5	31.5	21.7
- 28	10.7	15.6	19.5	14.4
- 35	8.5	11.5	13.3	11.2
- 48	6.8	8.6	9.1	7.8
- 65	5.4	6.5	6.2	5.6
-100	4.3	4.9	4.1	4.0

Table 5d

15 Minutes -6+8	-8+10	-10+14	All+14
100.0			99.8
67.8	100.0		88.9
44.5	73.2	100.0	69.6
29.6	47.6	68.2	48.0
23.0	34.5	47.3	35.4
17.7	24.8	31.1	24.5
14.1	18.5	22.0	19.2
11.4	14.0	15.3	13.7
9.0	10.4	10.5	10.1
7.2	7.8	7.2	7.4

TABLE 6. Effect of Feedstock Size Range and Number of 0.5 Inch Steel Balls on the Final Product Size Distribution (5 Minute Run Time; Cory Division Granular Product)

Table 6a

Mesh	15 Balls -6+8	-8+10	-10+14	All+14
- 6	100.0			98.9
- 8	16.1	100.0		68.5
- 10	5.8	17.2	100.0	29.9
- 14	2.9	6.6	12.5	8.1
- 20	2.0	3.9	5.6	4.4
- 28	1.4	2.4	2.9	2.8
- 35	1.0	1.7	1.7	1.8
- 48	0.8	1.2	1.1	1.3
- 65	0.5	0.9	0.7	0.9
-100	0.4	0.7	0.4	0.6

Table 6b

Mesh	20 Balls -6+8	-8+10	-10+14	All+14
- 6	100.0			98.8
- 8	24.0	100.0		66.5
- 10	9.1	24.5	100.0	30.3
- 14	4.8	10.1	17.4	10.9
- 20	3.2	6.1	7.9	6.2
- 28	2.3	3.9	4.4	4.1
- 35	1.7	2.7	2.5	2.8
- 48	1.2	1.9	1.6	2.1
- 65	0.7	1.5	1.0	1.6
-100	0.5	1.1	0.5	1.1

Table 6c

Mesh	25 Balls -6+8	-8+10	-10+14	All+14
- 6	100.0			98.9
- 8	30.3	100.0		72.0
- 10	13.0	33.2	100.0	38.3
- 14	7.3	14.4	22.9	15.5
- 20	5.1	8.7	11.3	9.0
- 28	3.7	5.9	6.3	6.1
- 35	2.8	4.1	3.7	4.1
- 48	2.0	3.0	2.4	3.1
- 65	1.2	2.2	1.5	2.3
-100	1.0	1.6	0.8	1.6

Table 6d

Mesh	30 Balls -6+8	-8+10	-10+14	All+14
- 6	100.0			99.2
- 8	34.8	100.0		77.4
- 10	15.8	39.9	100.0	44.8
- 14	9.1	19.0	28.0	20.6
- 20	6.4	12.2	14.1	12.3
- 28	4.7	8.1	8.1	8.3
- 35	3.6	5.7	4.9	5.7
- 48	2.7	4.2	3.0	4.2
- 65	1.8	3.1	1.9	3.0
-100	1.5	2.3	1.0	2.1

Table 6e

Mesh	35 Balls -6+8	-8+10	-10+14	All+14
- 6	100.0			99.2
- 8	41.8	100.0		76.9
- 10	19.9	45.3	100.0	46.6
- 14	11.2	23.0	33.2	23.5
- 20	7.8	15.0	17.6	14.7
- 28	5.8	10.1	10.2	10.1
- 35	4.5	7.2	6.2	7.0
- 48	3.4	5.3	3.7	5.3
- 65	2.3	3.8	2.4	3.8
-100	1.8	2.9	1.3	2.6

TABLE 7. Effect of Feedstock Size Range and Steel Grinding Ball Diameter on the Final Product Size Distribution (25 Balls; 5 Minute Run Time; Cory Division Granular Product)

Table 7a

Mesh	3/8 Inch -6+8	-8+10	-10+14	All+14
- 6	100.0			97.9
- 8	6.2	100.0		57.9
- 10	1.0	7.0	100.0	16.7
- 14	0.5	1.7	7.3	2.2
- 20	0.3	0.9	3.0	1.2
- 28	0.3	0.6	1.3	0.8
- 35	0.2	0.4	1.2	0.7
- 48	0.1	0.3	0.4	0.5
- 65	0.1	0.3	0.3	0.7
-100	0.1	0.2	0.3	0.3

Table 7b

Mesh	1/2 Inch -6+8	-8+10	-10+14	All+14
- 6	100.0			98.9
- 8	27.5	100.0		69.0
- 10	11.9	33.2	100.0	33.9
- 14	6.3	14.4	31.6	14.3
- 20	4.4	8.7	15.7	8.7
- 28	3.3	5.9	9.1	6.9
- 35	2.6	4.1	6.1	4.5
- 48	2.0	3.0	4.0	3.2
- 65	1.6	2.2	2.3	2.7
-100	1.2	1.6	2.0	1.6

Table 7c

Mesh	5/8 Inch -6+8	-8+10	-10+14	All+14
- 6	100.0			99.6
- 8	69.7	100.0		87.6
- 10	45.4	69.2	100.0	63.6
- 14	27.8	42.4	65.5	39.9
- 20	20.3	29.0	42.1	27.3
- 28	15.4	20.7	28.0	19.6
- 35	11.8	15.0	19.1	14.5
- 48	8.9	10.9	13.1	10.4
- 65	7.0	8.2	7.6	8.4
-100	5.3	6.0	6.2	5.1

CANPOTEX BALL MILL DEGRADATION TEST STANDARD FOR GRANULAR OR COARSE PRODUCT

EQUIPMENT

1. A stainless steel ball mill container, 7.5 inches in diameter by 2.5 inches wide, with 6 flights 0.5 inches high, equally spaced around the internal circumference of the chamber.

   The ball mill is driven by a gear motor at 33.4 rpm.

2. 25 steel balls, 0.5 inches in diameter, total weight of 208.2 grams. The balls should be stored in methanol when not in use to prevent rusting.

3. Tyler mesh screens full height stainless steel 8 mesh, 10 mesh, 20 mesh and a scalping screen larger than 8 mesh but smaller than 0.5 inch. These screens should be reserved for degradation tests and should be washed periodically to prevent build-up of reagents and potash.

4. Rotap* shaker with a hammer.

5. Automatic timer to start and stop equipment in a 5.0 minute test interval.

PROCEDURE

1. Split the representative potash sample to obtain 100 to 150 grams of -8+10 mesh material. Screen on the Rotap with the hammer down using the 8 and 10 mesh screens for 5.0 minutes.

2. Weigh 100 grams of the -8+10 mesh productand transfer it to the ball mill container. It is essential that exactly 100 grams of product ends up in the ball mill container.

3. Add the 25 steel balls.

4. Rotate the ball mill for 5.0 minutes at 33.4 rpm.

5. Transfer the contents of the ball mill container to the scalping screen. The scalping screen is placed on top of the 20 mesh screen to retrieve the steel grinding balls.

6. Remove the scalping screen. Screen the contents of the 20 mesh screen on the Rotap shaker for 2.0 minutes with the apparatus hammer down.

7. Weight the contents of the 20 mesh screen.

8. Calculate (Percent Degradation) = (100%) - (Mass in grams of potash product retained on 20 mesh screen) = Degradation Index.

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* Rotap is the trade name of a screen shaker apparatus Testing Sieve Shaker Model B supplied by the C.E.Tyler Company.

Participant comments on aspects of this test form an important part of the project record:

The mill chamber design is similar to that of a TVA apparatus (3), although improvements have been made in machining detail. Distortion can occur in the right cylinder when flights are welded in place, which may cause a poor lid-to-cylinder seal. Final machining of the container rim will guarantee a true fit and containment of fines.

The rotation speed of the electric motor drive was specified to be 30 rpm. The average value for the motors installed on these units was 33.4 rpm. As the degradation index was found to vary linearly with time of rotation of the mill, conversion of data to any specified number of chamber revolutions would be acceptable. The test as adopted by member companies will continue to use 33.4 rpm x 5.0 minutes = 167 revolutions as the reporting basis.

Users were advised that chamber or steel ball wear might affect test results in the longer term, and condition of the test equipment should be inspected periodically.

Screen wear may also contribute experimental error. Although the procedure does not require it, the use of new stainless steel mesh Tyler screens was a recommended practice.

Any electric or mechanical timer used for automatic control of the mill motor should be checked for accuracy. One such device used in this campaign was found to be significantly in error.

The selection of a 100 gram sample of the -8+10 size fraction was considered to yield an acceptable degradation index. However, concern was expressed by some participants that this -8+10 fraction might not be representative of potash products if the trend towards larger product sizes (SGN numbers) continued. In addition, routine testing of smaller size range coarse grade materials would be more difficult

if screening to obtain 100 g of test feed of -8+10 mesh required an excessive quantity of field sample. Participants accepted that other feed screen sizes could be selected for either special or internal company purposes. However, the standard test procedure would only permit reporting of degradation indexes based on -8+10 mesh feed for Canpotex shipments.

No pre-test treatment of samples (eg. drying) is specified. Potash materials are required to be "representative" of the source product, and use of accepted sampling and sample reduction practices to acquire laboratory portions is expected. Becase the test needs a narrow size range (-8+10 mesh) of material, riffling of the fraction is not necessary. The selection of product with or without loadout reagent treatment is acceptable, although degradation index values will be lower in the former case.

Test step 7 requires the material retained on the 20 mesh screen to be weighed for input to the calculation of step 8. All other solids may be weighed as a check on the overall mass balance of the experiment.

Experience with the Standard Ball Mill Product Degradation Test

There was general agreement that the apparatus was easy to use and the procedure was simple, fast and reproducible. The independent evaluations of degradation index dependence on test variables indicated that results were linearly dependent on parameter changes. Consistent results can be obtained in all laboratories with different technicians. This ball mill test was found to have overall advantages compared to other procedures.

The test could distinguish among reference materials used in the round-robin trials. However, concern was expressed that high degradation index values for natural crystal vs compacted product did not complement actual experience with the former type of product in the field.

TASK TWO: PRODUCT PERFORMANCE IN THE LABORATORY AND OFFSHORE ENVIRONMENTS

Background

Fertilizer products including potash materials are known to be sensitive to changes in humidity and to mechanical stress which may contribute to dissolution-crystallization cycles or particle size reduction and dust formation respectively. These conditions are likely to be encountered when granular potash produced in Saskatchewan is exported over long distances with frequent intermodel transfers to tropical or subtropical destinations. Correlations between moisture levels and abrasion resistance have been investigated and data from Cominco are included in Appendix IV. Technology developed by potash companies has established appropriate process conditions and protective surface conditioners for production of quality products in Saskatchewan.

To achieve further improvement in these practices, project participants recognized the need for laboratory test methods that would simulate or accelerate the offshore environmental conditions and facilitate the measurement of any adverse effects. Improvements were desired in both dust formation and product caking tests to improve reliability and reproducibility as a prerequisite to evaluation of the effectiveness of alternative dedusting and anticaking reagent treatments.

The work reported in this section was completed based on laboratory procedures developed by Wist of PCS, and others. Where experiments with chemical reagents either yielded results of proprietary value to Saskatchewan producers, or suggested a ranking of the performance of reagents contributed by suppliers to the industry, or inferred superiority of one participant's potash product over others, the materials have been assigned generic identifications. These details will be disclosed to project participants on request but are excluded from this report.

Dedusting Test Development

Various apparatus designs have been used to collect dust or air-entrainable particulates present in fertilizer products (2). Removal of

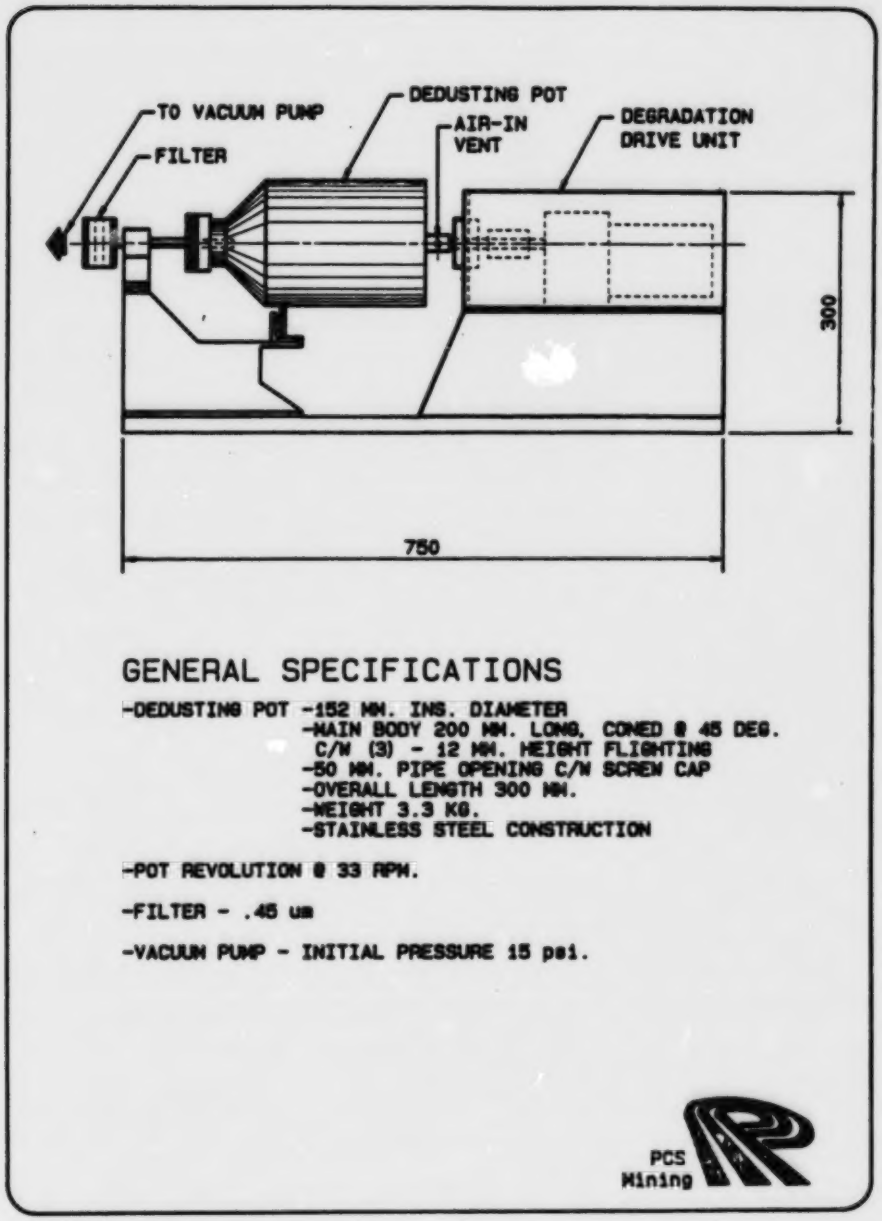

TO VACUUM PUMP
FILTER
DEDUSTING POT
AIR-IN VENT
DEGRADATION DRIVE UNIT
300
750
GENERAL SPECIFICATIONS
-DEDUSTING POT -152 MM. INS. DIAMETER
-MAIN BODY 200 MM. LONG, CONED @ 45 DEG. C/W (3) - 12 MM. HEIGHT FLIGHTING
-50 MM. PIPE OPENING C/W SCREW CAP
-OVERALL LENGTH 300 MM.
-WEIGHT 3.3 KG.
-STAINLESS STEEL CONSTRUCTION
-POT REVOLUTION @ 33 RPM.
-FILTER - .45 um
-VACUUM PUMP - INITIAL PRESSURE 15 psi.
PCS Mining

Figure 2. Design of the PCS Dedusting Test Equipment

dust by air classification or screening, with or without simultaneous abrasion or impact degradation, has been the preferred approach in these procedures. Participants in the initial planning meeting for this project concluded that tests which had been evaluated for potash applications were not yet satisfactory.

A significant improvement has been achieved by Wist of PCS in the form of the dedusting test equipment illustrated in Figure 2 and the procedure described below. The stainless steel dust generation and entrainment chamber is an accessory for the Degradation Test assembly discussed in the previous section of this report. Entrained dust is collected on a removable filter disk holder for easy measurement. The superiority of this method over the previous generation of equipment used by PCS is demonstrated by the two following sets of data:

TABLE 8. COMPARISON OF THE OLD AND NEW PCS DEDUSTING TESTS

Test Datum	Old Test	New Test
Reference Product	Potassium sulphate	Potassium sulphate
Type	Granular	Granular
Number of Trials	4	10
Test Results, ppm	2591 3597 5293 4445	1343 1469 1554 1433 1433 1447 1382 1475 1330 1497
Average Value, ppm	3981	1436
Standard Deviation, ppm	1002	66
Range, ppm	2591 to 5293	1330 to 1554

The magnitude of the Dedust Test Index in units of parts per million, ppm, is about three times lower suggesting reduced particle damage. The standard deviation is substantially lower for a series of ten trials. The redesigned test chamber allows only very fine dust to be trapped in the filter assembly, thereby avoiding carryover of large particles.

The effect of the steel ball size and number used to mill Granular SGN 210 potash (KCl) test material was evaluated. Table 9 summarizes the results of nine experiments:

TABLE 9. EFFECT OF BALL MILL VARIABLES ON DEDUSTING TEST

Steel Balls Used		Dust Collected
Number	Diameter, inches	ppm
100	1/2	26,900
75	3/8	5,725
50	3/8	3,642
50	5/16	1,928
50	5/16	1,892
50	5/16	1,792
50	5/16	1,788
50	5/16	1,878
50	5/16	1,999

The subset of six trials using 50 x 5/16 inch diameter steel balls had an average of 1879 $\pm$ 74 (sigma) ppm. The following procedure is recommended based on these data.

Dedusting Test Procedure

For Granular potash products:

1. Screen the product and retain +14 Tyler mesh material.

2. Transfer a 200 g sample of the +14 mesh material to the dedusting test container. Add fifty 5/16 inch diameter steel balls.

3. Weigh the removable filter accessory.

4. Start air flow through the assembled apparatus and adjust the pressure drop to 15 psig. This setting applies when a Gast air pressure/vacuum, rotary, motor-mounted type pump supplied by Western Scientific is used to purge the chamber.

5. Rotate the container for 15 minutes with continuous air flow to entrain and filter dust that is generated by milling.

6. Remove and weigh the filter apparatus, calculate and report the Dedusting Index in parts per million (ppm) of the initial test material.

7. Wash the chamber with methanol solvent after tests with reagentized products.

For Special Standard or Suspension grades of potash (KCl) products, follow the steps listed above without addition of the steel milling balls.

Note that excess humidity may lower the Dedusting Index, presumably because of agglomeration of dust particles in the test apparatus. Direction of a warm air flow (eg. from a car warmer) onto the outside of the milling chamber was found to be effective in reducing the relative humidity of entrainment air.

Dedusting Test Indices for Different Granular Products

Granular potash (KCl) products from five different sites were screened to obtain the Size Guide Number (SGN) and Uniformity Index (UI) and were tested according to the dedusting procedure described above. The results presented in Table 10 show that four products responded in the same way while one exhibited a significantly lower Dedusting Index. The potash samples were all unreagentized and were not predried before testing.

TABLE 10. COMPARISON OF DEDUSTING INDICES FOR FIVE POTASH PRODUCTS

Product Source	SGN	UI	Dedust Index ppm
A	220	40	1511
B	220	42	1058
C	295	127	1590
D	280	139	1558
E	245	40	1476

Anticaking Test Development

The tendency of moisture sensitive potash materials to cake or set up in bags, silos, hopper cars, ship holds or warehouses is well known within the fertilizer industry. When free-flowing granular potash transforms into a solid porous mass, product handling may require extreme remedial measures. Even heavy equipment may become ineffective for penetration of caked piles of potash.

Induction of product caking in the laboratory by creation of conditions which simulate the heat and moisture transport or product segregation and compaction that can occur between the minesite and the customer has been investigated for decades (2,3). A universally satisfactory test method does not yet exist, although each potash producer has adapted variations of laboratory procedures described by Hoffmeister (2). A reliable, reproducible test is a prerequisite for evaluation of the effectiveness of chemical additives, so-called anticaking or dedusting reagents, that are used within the industry to minimize the potential for potash product caking.

Wist, Chief Chemist at PCS, has evolved a procedure with the objective of exposing potash materials in the Granular to Standard size ranges to a controlled set of time interval, moisture, temperature, compaction and fracture test conditions. The results described below show that progress has been made towards establishing a reliable laboratory anticaking test.

Anticaking Test Procedure and Results

In initial trials, two series of experiments were completed using an SGN 210 Granular product. After drying at 400°C, each set of 8 samples was exposed to moisture in a closed container at humidity levels set by the vapour pressure of either saturated sodium hydrogen orthophosphate ($Na_2HPO_4.12H_2O$) or saturated sodium chloride brines. The relative humidity (RH) above each brine was measured and found to be 95% and 75.4% respectively. Each sample was loaded into right cylinder split ring molds and held under piston-applied pneumatic pressure of 40 psi for 3 days at ambient temperature. After this period, 4 samples from each set were loaded to the point of failure in an hydraulic press. The temperature of the remaining samples was raised to 40-45°C for 1 day, after which the failure loads of pressed disks were measured. Initial moisture levels of the sixteen test samples were determined before compression in the caking cells, and composite moistures were measured after the breaking test, by the gravimetric method. The results are summarized in Table 11.

TABLE 11. MOISTURE AND TEMPERATURE CYCLE AND FAILURE LOADS FOR GRANULAR SGN 210 IN THE PCS ANTICAKING TEST

Experimental Data	Series 1		Series 2	
Caking Chamber Temp., °C	20	20,40	20	20,40
Total Number of Trials	4	4	4	4
Mass of Potash per Trial, g	70	70	70	70
Relative Humidity, %				
Above Brine	95	95	75	75
Above Samples	83	83	68	68
Product Moisture, ppm				
Pre-test	750	750	510	510
Post-test	270	220	190	150
Caking Pressure, psi	40	40	40	40
Pellet Failure Load, lbs	321	501	0	0
Range, lbs	310-330	475-540		

A similar series of caking trials was completed using a Suspension grade potash product. The material was used as received and was not predried at elevated temperature. The results are summarized in Table 12.

TABLE 12. MOISTURE AND TEMPERATURE CYCLE AND FAILURE LOAD FOR SUSPENSION GRADE PRODUCT IN THE PCS ANTICAKING TEST

Experimental Data	Series 1	Series 2
Caking Chamber Temp., °C	20	20,40
Total Number of Trials	4	4
Mass of Potash per Trial, g	70	70
Relative Humidity, %		
Above Brine	95	95
Above Samples	83	83
Product Moisture, ppm		
Pre-test	1550	1650
Post-test	590	570
Caking Pressure, psi	40	40
Pellet Failure Load, lbs	620	998
Range, lbs	470-690	890-1040

The data reported in Tables 11 and 12 suggest that exposure of potash materials to controlled moisture, temperature, and loading cycles can induce reproducible caking in reference materials. When the measured relative humidity to which samples are exposed was below the potash critical relative humidity (CRH) of 70 to 84% (2,5), the Granular product did not cake under the test conditions. Heating the air in the test chamber to about 40°C increased the pellet strength significantly, partly because of further reduction of moisture in the final material.

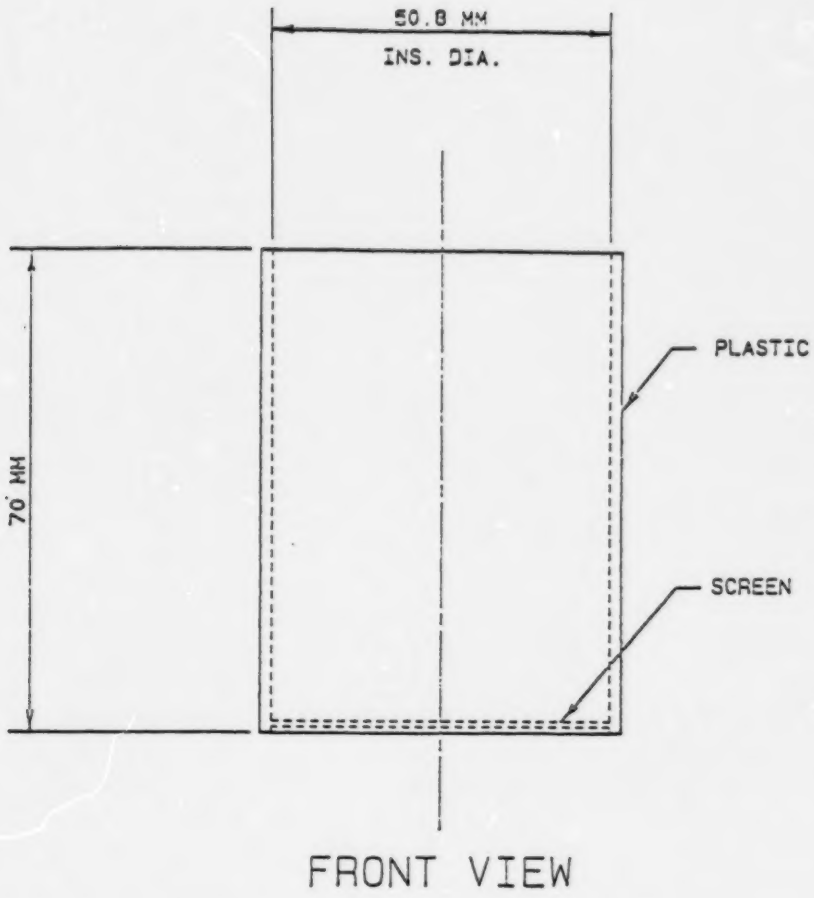
The fine Suspension grade product had both a greater moisture uptake and loss cycle and higher failure loads for caked pellets than those of the Granular product noted in Table 11.

Anticaking Test Procedure for Granular Product

The following procedure was used to obtain the data reported in the previous section, and to provide a relative performance evaluation of a series of anti-caking treatments discussed in the next section. Aspects of the test continue to be improved. This interim procedure should not be adopted as a standard until a more broadly based assessment of reliability has been completed.

ANTICAKING PROCEDURE FOR GRANULAR PRODUCT (PRELIMINARY)

1. Screen the granular product to +14 mesh.
2. Heat the product to 350°C for 24 hours to eliminate initial moisture and reagents.
3. Store the product at 70°C until ready for use.
4. Reagentize the product in a heated mixer keeping the temperature of the product between 60°C and 70°C. Mix for 15 minutes.
5. Store the reagentized product in sealed glass jars for 7 days.
6. Moisturize 80 grams of product for 6 hours in the humidifier using the standard porous jars shown in Figure 3. The vapour pressure is set by a saturated solution of sodium hydrogen orthophosphate ($Na_2HPO_4.12H_2O$). Record the relative humidity in the closed chamber after each hour.
7. Load 70 g of sample into each anticaking press and leave under load for 3 days at 40 psi and room temperature. Measure moisture by gravimetric test at 70°C on the remaining 10 grams of product.
8. After 3 days in the presses, increase the temperature in the anticaking cabinet to 40°-45°C and leave for 1 day.
9. Break the resulting briquettes on the hydraulic press and record the force in pounds required to break each pellet.
10. Measure residual moisture of each fractured sample using the gravimetric method at 70°C.



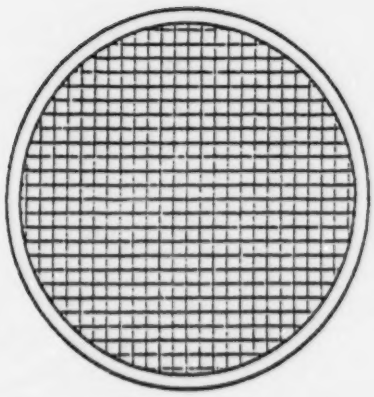


Figure 3. Design of sample containers used to contain potash product in humidifier chamber

Anticaking and Dedusting Indices for Different Product Treatments

Samples of a Granular SGN 210 product were treated with eleven different combinations of commercially available anticaking and dedusting reagents. Table 13 lists the combinations of additives. This set of treated materials was used to evaluate the capability of both the tests described above to detect differences in the anticaking and dedusting characteristics of treated potash product.

All samples were treated on the same day with up to 1.1 kg/t of additives and stored in sealed glass containers. Because only eight samples could be run through the test sequence at one time, the full set of trials extended over a 44 day period. This delayed evaluation of samples yielded data on the time dependence of reagent effects. Anticaking Indices entered below under test series 1 to 3 were determined at similar increasing time intervals after treatment.

Table 14 summarizes the results from both anticaking and dedusting tests for each reagent treatment. One untreated SGN 210 sample was included for comparison. The three columns under each anticaking trial include pre- and post-test moisture levels and the pellet failure load. Note that several reagent combinations exhibited significantly increased anticaking performance with longer pre-test storage, eg. cases 3, 4, 5, and 8. Others yielded poorer anticaking results at longer times, eg. 9 and 10.

The two columns of dedusting test values were collected during experiments separated by a 20-day time interval. In every case the treated product was superior to the untreated Granular SGN 210. Within the set, certain additives (eg. cases 3, 4 and 5) showed improved dedusting properties after longer pre-test storage. One reagent (#9) caused a large increase in the Dust Index, indicating deterioration of the sample properties with time.

These results suggest that after further refinement of the details of the Anticaking and Dedusting procedures presented above that laboratory data may become more valuable not only for characterization of potash products before shipment, but also to assist with the prediction of product

behaviour while in the offshore distribution network. Better control of the experimental conditions and improved design of test equipment has yielded more reproducible data than has previously been reported. These procedures may be acceptable for adoption as standard potash industry tests after round-robin assessment.

TABLE 13. REAGENT TREATMENTS EVALUATED FOR ANTICAKING AND DEDUSTING EFFECTIVENESS ON GRANULAR SGN 210 PRODUCT

Sample	Reagent Added			
	Anticake Reagent	kg/t	Dedustant	kg/t
1	-	0	-	0
2	Amine	0.1	Refined oil	1.0
3	Neutralized Amine	0.1	Refined oil	1.0
4	Neutralized Amine	0.1	Refined oil	1.0
5	Amine	0.1	Refined oil	1.0
6	Diamine	0.1	Refined oil	1.0
7	Amine	0.1	Refined oil	1.0
8	-	0	Proprietary Chemical Blend	1.0
9	-	0	Organic Sulfonate Blend	1.0
10	-	0	Proprietary Wax Blend	1.0
11	Amine Mixture	0.1	Refined oil	1.0
12	Amine	0.1	Refined oil	1.0

TABLE 14. RESULTS OF THREE ANTICAKING TESTS AND TWO DEDUSTING TESTS ON TREATED SAMPLES OF GRANULAR SGN 210 POTASH PRODUCT

RESULTS:

RUN #	ANTICAKING TEST #1			ANTICAKING TEST #2			ANTICAKING TEST #3			DEDUST TEST PPM	
	H2O(1)	H2O(2)	lbs	H2O(1)	H2O(2)	lbs	H2O(1)	H2O(2)	lbs	OCT 30	NOV 20
1.	.179	.000	570	.173	.015	820	.266	.016	880	1879	1842
2.	.202	.013	380	.180	.017	320	.283	.019	260	397	336
3.	.173	.008	400	.139	.017	400	.204	.026	120	351	19
4.	.168	.013	200	.166	.021	80	.176	.024	0	365	6
5.	.182	.008	300	.162	.010	160	.185	.027	60	240	136
6.	.167	.010	410	.174	.016	310	.178	.029	290	311	334
7.	.163	.011	440	.175	.015	370	.182	.022	300	585	522
8.	.174	.006	720	.166	.012	560	.183	.016	370	866	861
9.	.177	.011	305	.189	.014	460	.243	.011	580	687	1516
10.	.103	.021	305	.128	.009	500	.186	.008	590	410	246
11.	.163	.018	0	.170	.011	0	.201	.017	20	394	246
12.	.189	.016	540	.149	.023	100	.238	.013	780	290	178

H2O (1): After exposure to water vapour at 95% RH
H2O (2): After breaking test
lbs: Failure load for sample pellet in pounds

Degradation and Dedusting Indices for USSR and GDR Potash Products

Two samples of competitors' product were evaluated using the test methods discussed in this report. These data should be compared with similar values for untreated Saskatchewan products presented in Tables 4 and 10. Note that high moisture levels affect test results.

TABLE 15. ANALYSIS OF OFFSHORE COMPETITORS' PRODUCTS

Property	Unit	Potash Source	
		USSR	GDR
K_2O	%	62.57	60.16
H_2O	ppm	600	5100
Amine*	kg/t	0	0.34
Oil	kg/t	1.29	0.79
SGN		235	290
UI		43	40
Degradation	%	7.8	10.0
Dedust Index	ppm	943	1020

* Reported as Armeen T equivalent

CHEMISTRY, PHYSICS AND MATERIALS SCIENCE OF POTASH PRODUCTS

Uncertainty About Product Quality

The main risk of using the results of laboratory standard tests to characterize the quality parameters of potash products is that the base of empirical data may not correctly represent the behaviour of these materials under actual product exposure conditions between production sites and customers. Only a positive correlation of laboratory data and field experience with product durability, flowability and customer satisfaction will provide confidence in the validity of test methods intended to simulate these environmental stresses. Until that base of information is in place, confidence in the use of test data to predict field performance and to modify processing, reagent treatments or handling and storage practices to improve and protect products will be limited.

To compensate for this uncertainty in the application of degradation, anticaking and dedusting indices produced for quality control purposes, it is valuable to consider the fundamental physical and chemical processes which affect the response of potash materials to moisture, temperature, reagents, and mechanical stress. By understanding these phenomena better, a theoretical framework can be established to relate laboratory observations to field experience with potash product. A capability to correctly interpret experimental results will contribute to Offshore Product Quality.

This section includes a discussion of potash materials and an explanation of the significance of the relevant chemistry, physics and materials science of potash materials. Reference is also made to the conceptual model of potash products (Figure 4) that summarized the empirical experience of project participants and associated product failure mechanisms.

Effect of Moisture on Potash Products

Because potash is comprised of two highly soluble salts, potassium chloride plus a minor amount of sodium chloride, the solid will readily dissolve when water is available in excess. Potash products are found to

be stable during handling and storage only because of a shortage of moisture in the surrounding environment. Even exposure to rain is not usually enough to dissolve large piles of product.

Interaction between moisture and the surfaces of potash particles is nevertheless extremely important in determining the resistance of the material to abrasion or impact, caking, and dust formation. In other words, moisture has a direct influence on the critical product attributes of durabilty and flowability that are important to customers.

Kaiho, Chikazawa and Kanazawa (6) studied the adsorption of water vapour on to sodium chloride powder and found that significant uptake of water (eg. 100 microgram per gram) occurred at water vapour partial pressures of 2 mm of mercury (equivalent to a relative humidity, RH, of 10 percent). Similar data are not available for H_2O on KCl, but we can assume that the response of KCl surfaces would resemble that of NaCl. Once several layers of water have adsorbed on the KCl surface, probably above 70% RH, the surface of KCl particles will effectively be covered by an extremely thin layer of brine, in the order of 1 mg/m^2.* The equilibria and dynamics of this thin surface brine film affects the properties of potash products as discussed below.

The uptake of water by granular potash materials has been observed frequently by manufacturers of these products. Data presented previously in this report confirm that steady-state condensed moisture levels of 100 to 1500 ppm or more are measurable within ambient RH limits of 15 to 90 percent. For example, in our anticaking experiments Suspension grade potash absorbed 1550 ppm of water and Granular grade absorbed 750 ppm of water when exposed to 95% RH at about 20°C. The decreased specific surface area (m^2/g) of these materials accounts for the difference in behaviour of the samples.

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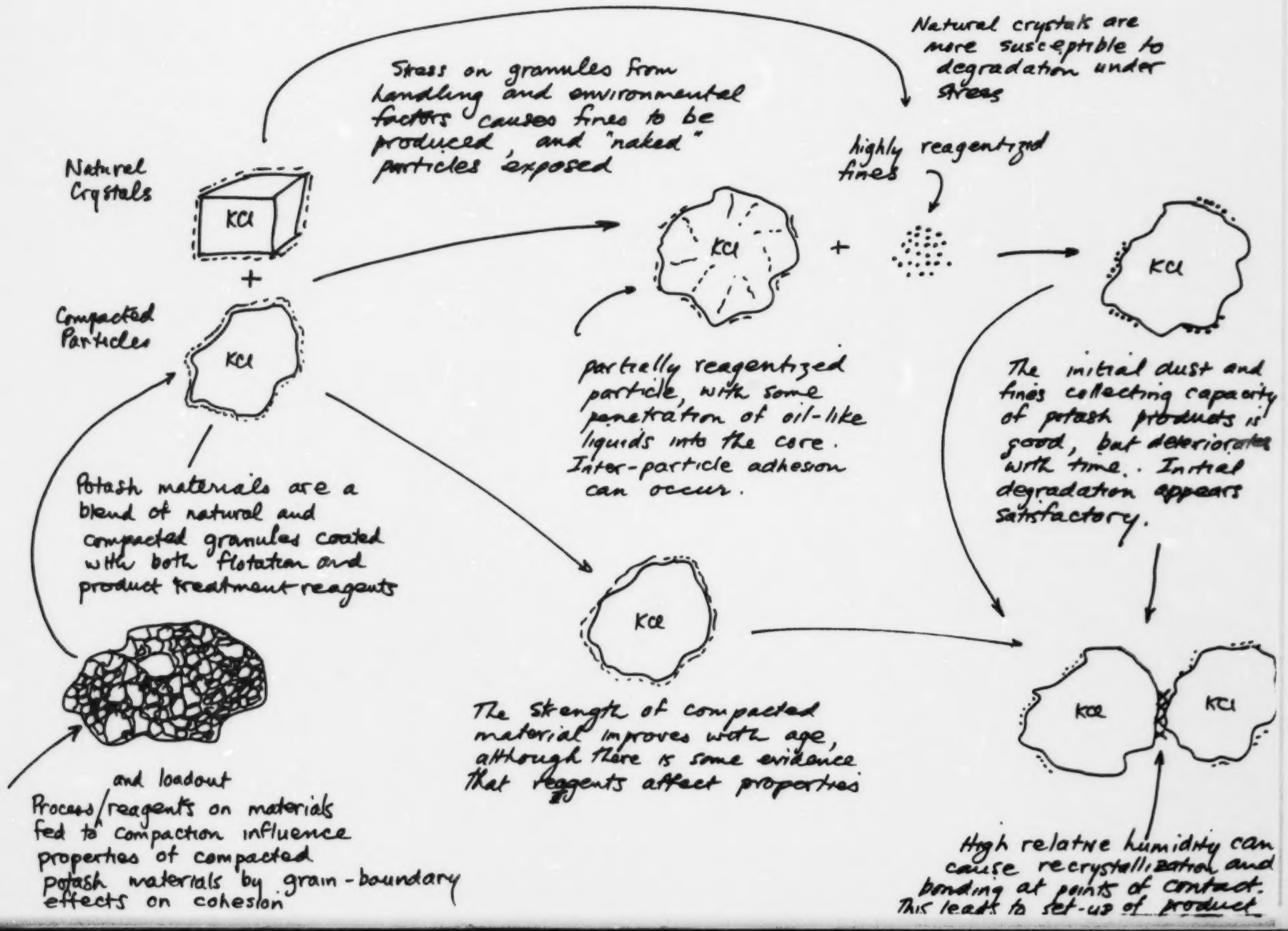
* At a typical moisture level of 0.03 percent (300 microgram/gram) and surface area of 0.3 m^2/g, the surface moisture level is about 1 mg/m^2.

Figure 4. CONCEPTUAL MODEL OF POTASH PRODUCTS.


Natural crystals are more susceptible to degradation under stress
Stress on granules from handling and environmental factors causes fines to be produced, and "naked" particles exposed
highly reagentized fines
Natural Crystals
KCl
+
Compacted Particles
KCl
KCl
+
KCl
partially reagentized particle, with some penetration of oil-like liquids into the core. Inter-particle adhesion can occur.
The initial dust and fines collecting capacity of potash products is good, but deteriorates with time. Initial degradation appears satisfactory.
Potash materials are a blend of natural and compacted granules coated with both flotation and product treatment reagents
KCl
KCl
KCl
The strength of compacted material improves with age, although there is some evidence that reagents affect properties
and loadout
Process/reagents on materials fed to compaction influence properties of compacted potash materials by grain-boundary effects on cohesion
High relative humidity can cause recrystallization and bonding at points of contact. This leads to set-up of product

The importance of the Critical Relative Humidity (CRH) point for potash and other soluble salts has been studied in an elegant way by Cohen, Flagan and Seinfeld using their electrodynamic balance. In their experiments, single micron-sized charged particles of KCl were freely suspended in an electric field. The increase in mass of a particle with increase of relative humidity in the experimental chamber was used to directly observe the CRH point at which rapid condensation of water vapour commenced to yield a KCl brine. The observed CRH for pure KCl was found to be 0.83 to 0.86 at 20°C, in agreement with values reported by Hoffmeister (2).

This characteristic of KCl and other highly soluble salts to reversibly absorb potentially large amounts of water is important to understanding the effect of moisture on potash. To illustrate the significance, consider a 1 tonne mass of granular KCl, containing a steady state quantity of 500 g (0.05%) adsorbed water. This surface layer will probably be saturated with both KCl and NaCl (deposited upon drying of process brine on to the solid) according to the expression for a co-saturated brine:

$$(KCl + NaCl),\ \% = 41.7 + 0.187\ T$$

where T = temperature in °C.

At 20°C the 500 g of moisture would contain 227 g of dissolved salts.

The quantity of KCl plus NaCl in this adsorbed water layer will change with condensation or evaporation of moisture, or with an increase or decrease of temperature. These cycles may cause the granular potash to cake or set up if the dissolved salts crystallize out at particle contacts in the reference 1 tonne porous mass of material.

It is probable that crystallization will occur selectively at these contacts because of the interaction of several physical and chemical phenomena. Condensation of water vapour will occur preferentially in the microporosity of the potash samples, including at surface microcracks, grain boundaries in compacted product, or most importantly at particle contacts between granules. The vapour pressure of water vapour P in equilibrium with a concave brine surface of radius of curvature r is

given by the expression (7a):

$$RT \ln (P/P^\circ) = 2 \gamma V/r$$

where R = Gas constant

T = Temperature, °K

P° = Normal vapour pressure of water at temperature T

γ = Surface tension of water

V = Molar volume of water

For example, the vapour pressure in a pore or crack of $r = 10^{-6}$ cm will be 11 percent lower than that of a free surface of water. This vapour pressure differential will provide the driving force for vapour phase transfer and condensation of moisture into fine cracks or pores. The same process will occur if the surface moisture is saturated with soluble salts. Thus, we should expect that more surface moisture will evaporate and condense in capillary-like structure of contact points present in assemblies of potash particles. The potential for product set up or caking by particle adhesion (8) or intergranular cementing by crystallization is enhanced by this capillary condensation phenomena. Adjorjan has discussed this salt bridging mechanism (14).

Spreading of Reagents on Potash Surfaces

Scanning electron microscope studies of the surfaces of potash particles have shown the highly irregular structure created by processing both natural crystal and compacted materials. Crushing and screening of potash yields complex cleavage patterns and random jointing at grain boundaries. Evaporated process brine and residual debris also contribute to surface roughness of particles. This surface state affects the behaviour of anticaking and dedusting reagents at the particle interface.

Numerous studies of liquid spreading on solid surfaces have illustrated the effects of surface irregularities on the behaviour of sessile microdroplets (7, 9-11). Both aqueous brine, and detergent solutions with low surface tensions, were found by Okawara and Kadota to exhibit significant contact angles of about 20 and 15 degrees respectively against potassium chloride (12). Contact angle studies by Strathdee and Kallur (13) have shown that the fatty acid, alcohol and amine reagent groups each have significant contact angles (15 ± 10 degrees) against KCl at relative humidities between 0 and 90 percent.

These data suggest that anticaking and dedusting treatments of potash products are unlikely to result in ideal uniform coverage of the exterior of particles. It is probable that organic reagents, typically of the long chain amine plus hydrocarbon oil classes, are distributed over the surface of potash granules as islands of microdroplets, constrained by both negative spreading coefficients (13) and sharp-edged surface microsteps. The possibility is high that unreagentized surfaces may contact one another throughout a mass of granular potash, and this would tend to facilitate interparticle condensation- evaporation processes leading to product deterioration, as discussed in the previous section of this report.

Slow secondary spreading of reagents by capillarity may contribute to the time dependent anticaking and dedusting results presented earlier in this report. First, creep or vapour phase transport of mixed reagents over the product surface would improve coverage and anticaking performance with time and affect moisture-limited processes. Second, penetration of fluids into the internal porosity of compacted particles would reduce the free liquid present on the external surface, thereby decreasing the capacity to wet and collect dust. Improved anticaking and loss of dedusting capability can each be explained by secondary reagent spreading.

Mechanisms of Anticaking Action

Alternative mechanisms of action of surface-active anticaking reagents are worth consideration when evaluating sets of laboratory test results. The long chain hydrocarbons with hydrophilic terminal functions such as the amino-, carboxy-, hydroxy, sulfonate and their corresponding acidic or basic forms are known to adsorb selectively at aqueous interfaces. The amine or ammonium salts of C_{14} - C_{18} fatty acids commonly used as anticaking additives for potash products may function as crystal growth modifiers which affect the morphology of KCl deposited at interparticle contacts. Poor adhesion of resulting material will effectively reduce the tendency of products to cake in storage.

In addition, monomolecular films of surfactants have been used as diffusion barriers on reservoirs to reduce the rate of evaporation of water (7b). It is possible that either residual flotation process amines or anticaking chemicals are acting in this way on a microscopic scale to reduce the rates of moisture transport within potash piles.

The significance of both these chemical processes will require experimental studies beyond the scope of conventional potash industry practices.

EXTENSION OF THE OFFSHORE PRODUCT QUALITY PROJECT

This report summarizes the work conducted under the project leadership of Graeme Strathdee Director, Research and Development, and Bill Wist, Chief Chemist, of the Potash Corporation of Saskatchewan.

By agreement of member companies of the SPPA and Canpotex, an extension of this study has commenced entitled "Product Degradation in Transit" and managed by Elmar Goldsmith and Joe Gosselin of Kalium Chemicals. Funding for this project is provided under the framework of an SPPA joint venture initiative, with supplementary input by CANMET, through the Canada/Saskatchewan Mineral Development Agreement.

Although each project is formally independent, in fact the steering committee of PCS, Kalium and Cominco representatives was common to each.

ACKNOWLEDGMENTS

The administrative assistance of Grant Feasby and others at CANMET, and of R.Boisselle and T.Ferguson the contract officers at Supply and Services Canada, is appreciated.

The generous co-operation of industry management at the participating companies PCS, IMC, Central Canada Potash, Cominco, Kalium Chemicals, PCA, and the interest of the Technical Committee of Canpotex is gratefully acknowledged.

The enthusiastic involvement of technical staff in the actively participating control laboratories ensured that this co-operative Offshore Product Quality Project was successful.

The technical staff of the PCS Pilot Plant are thanked for their contributions to equipment design, fabrication, and evaluation, for experimental test development, and for the many analyses required to support this study.

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APPENDIX I

CANPOTEX PRODUCT DATA SHEETS

Canpotex Limited

Potash

Product Grades

1. Standard
2. Special Standard
3. Coarse
4. Granular
5. White Soluble 1.0%
6. White Soluble 0.5%
7. Refined Chemical White Soluble

1 Standard Muriate of Potash

CHEMICAL ANALYSIS

Component/Equivalent	Symbol	Typical %
Potassium Chloride	KCl	96.3
Potassium Oxide	K_2O	60.8
Potassium	K	50.5
Moisture	H_2O	.2
Magnesium	Mg	<.1
Calcium	Ca	<.1
Sodium Chloride	NaCl	3.0
Sodium	Na	1.2
Chloride	Cl	47.6
Sulphate	SO_4	<.1
Water Insolubles		.4

PARTICLE SIZE DISTRIBUTION

Tyler Mesh	Symbol	Typical Cumulative %
Retained on 14 mesh	+14	15
on 28 mesh	+28	63
on 65 mesh	+65	96
Passing through 65 mesh	−65	4

PHYSICAL PROPERTIES

Parameter	Unit	Typical %
Bulk density	lbs/cbft	67
	kg/m^3	1075
Angle of repose	degrees	31

The symbol "<" signifies "less than"

2 Special Standard Muriate of Potash

CHEMICAL ANALYSIS

Component/Equivalent	Symbol	Typical %
Potassium Chloride	KCl	95.3
Potassium Oxide	K_2O	60.2
Potassium	K	50.0
Moisture	H_2O	.2
Magnesium	Mg	<.1
Calcium	Ca	<.1
Sodium Chloride	NaCl	3.0
Sodium	Na	1.2
Chloride	Cl	47.6
Sulphate	SO_4	<.1
Water Insolubles		.4

PARTICLE SIZE DISTRIBUTION

Tyler Mesh	Symbol	Typical Cumulative %
Retained on 28 mesh	+ 28	3
on 35 mesh	+ 35	15
on 48 mesh	+ 48	48
on 65 mesh	+ 65	63
on 150 mesh	+150	93
Passing through 150 mesh	−150	7

PHYSICAL PROPERTIES

Parameter	Unit	Typical
Bulk density	lbs/cbft	68
	kg/m^3	1090
Angle of repose	degrees	31

The symbol "<" signifies "less than"

3. Coarse Muriate of Potash

CHEMICAL ANALYSIS

Component/Equivalent	Symbol	Typical %
Potassium Chloride	KCl	96.5
Potassium Oxide	K_2O	61.0
Potassium	K	50.6
Moisture	H_2O	.2
Magnesium	Mg	<.1
Calcium	Ca	<.1
Sodium Chloride	NaCl	2.9
Sodium	Na	1.2
Chloride	Cl	47.7
Sulphate	SO_4	<.1
Water Insolubles		.4

PARTICLE SIZE DISTRIBUTION

Tyler Mesh	Symbol	Typical Cumulative %
Retained on 8 mesh	+ 8	6
on 10 mesh	+10	30
on 14 mesh	+14	80
on 20 mesh	+20	97
on 28 mesh	+28	97
Passing through 28 mesh	−28	2

PHYSICAL PROPERTIES

Parameter	Unit	Typical
Bulk density	lbs/cbft	67
	kg/m^3	1075
Angle of repose	degrees	33

The symbol "<" signifies "less than"

4 Granular Muriate of Potash

CHEMICAL ANALYSIS

Component/Equivalent	Symbol	Typical %
Potassium Chloride	KCl	96.1
Potassium Oxide	K_2O	60.7
Potassium	K	50.4
Moisture	H_2O	.2
Magnesium	Mg	<.1
Calcium	Ca	<.1
Sodium Chloride	NaCl	2.9
Sodium	Na	1.1
Chloride	Cl	47.4
Sulphate	SO_4	<.1
Water Insolubles		.4

PARTICLE SIZE DISTRIBUTION

Tyler Mesh	Symbol	Typical Cumulative %
Retained on 6 mesh	+ 6	7
on 8 mesh	+ 8	55
on 10 mesh	+10	88
on 14 mesh	+14	97
on 20 mesh	+20	98
Passing through 20 mesh	−20	2

PHYSICAL PROPERTIES

Parameter	Unit	Typical %
Bulk density	lbs/cbft	64
	kg/m^3	1025
Angle of repose	degrees	33

The symbol "<" signifies "less than"

APPENDIX II

SPPA MASTER PROPOSAL ON OFFSHORE PRODUCT QUALITY

RESEARCH & DEVELOPMENT PROPOSAL ON OFFSHORE PRODUCT QUALITY

OBJECTIVE

To improve the quality of Saskatchewan potash products delivered to the export market by:

(1) scientific investigation of the relationship between the processing of potash, reagent treatment of products, and the environmental conditions of humidity and temperature to which exported potash products are exposed;

(2) evaluation of standard testing procedures used by producers with emphasis on sampling of shipments, product size distribution, and potash degradation measurements;

(3) cooperation with the Canpotex Technical Committee on defining problems with product quality and recommendations for industry-wide action.

SCOPE OF WORK

Export Product Performance

Experimental techniques developed by the potash industry for determination of caking, degradation, and segregation of potash materials during shipment and storage will be applied to study the effect of environmental conditions on export product performance.

For example, product from Saskatchewan producers will be exposed to humidity and temperature cycles in the laboratory. Compaction tests and microanalytical methods will be used to measure the extent and consequences of product caking. These data will provide a better understanding of environmental effects on potash product performance and a quantitative basis for recommending changes in handling methods and reagent treatment.

Laboratory studies will be supplemented by analyses of samples received from storage and transfer points in the export market distribution system. Records of the exposure of selected shipments to humidity and temperature cycles will be acquired to select experimental conditions for the laboratory studies.

Product Testing Procedures

To contribute to an improved ability to meet Canpotex export product specifications, the capability of producers to analyze potash shipments will be compared by expending the scope of round-robin analyses of reference batches of products. Priority will be given to analyses of particle size distributions and product degradation.

The relevance of standard tests to the needs of the export market for product testing will be evaluated. Supplementary testing procedures and equipment developed by PCS Mining may be transferred to the industry as part of this project. In particular, the automatic particle size analyzer will be assessed as a device to rapidly measure size distribution of products at remote locations where laboratory analyses cannot be completed.

Evaluation of Anticaking and Dedusting Reagents

Subject to the agreement of participating companies, one or more laboratories will determine the effectiveness of different reagent treatments applied for the export market. Possible chemical or physical interactions among products treated with different reagent classes will be evaluated in standard anticaking and dedusting tests.

A base of consistent data will be issued to participants for the purpose of comparing the performance of treated product under conditions typical of the export market.

Project Cost

Labour	30 000
Materials and Supplies	2 500
Equipment	2 500
Consultants	5 000
Travel	5 000
Contingency	5 000
Total	50 000

APPENDIX III

SUMMARY OF MEETING #1,

OFFSHORE PRODUCT QUALITY PROJECT

OFFSHORE PRODUCT QUALITY PROJECT

SUMMARY OF MEETING #1

1. OPENING DISCUSSION ON PROJECT OBJECTIVES AND SCOPE

The background to the project was explained and the technical proposal was reviewed (Strathdee, PCS Mining).

Quality requirements for potash products marketed by Canpotex were reviewed (McMunn). Generally, particle size distribution, product colour and cost are important factors. For certain special customers, levels of minor or trace elements and anticaking and dedusting treatments need attention.

Quality potash product meets chemical composition and particle size distribution specifications, is free-flowing and is durable. These characteristics are required when received by the customer. It is not good enough to meet quality specifications at the production site. The customer determines acceptable quality.

Major Canpotex operating problems include (i) lack of control over materials handling in Vancouver (ship loading rates may be 1000 t/h, and unloading rates up to 2000 t/h); (ii) difficulty in sampling of product that is representative of shipments; (iii) comingling of product from different sources and segregation of material in storage; (iv) contamination of shipments by residues in railcars.

At the customer, there are relatively more problems with Granular and Coarse material than with Standard. The fate of reagents in applications cause some problems such as oil release in rice paddies or interference in chloralkali electrochemical processes.

Competitors' products are improving. Some granular products exhibit less breakdown and are more uniform in size. Some suppliers screen product upon arrival at destination to enhance acceptability.

The question about the relevance and validity of mine-site testing procedures to achieving downstream product quality was addressed. For example, do product degradation tests expose materials to great enough handling stress? Do these tests accurately evaluate compacted and natural crystal materials for abrasion and impact resistance? Are tests which provide information for process control good enough for predicting field performance of potash products?

Concepts such as acceptable product degradation within the Canpotex particle size range limits were considered.

The scope of the project does not include sampling or segregation topics, both of which are significant factors in managing product quality. These subjects need co-ordination and attention outside this project framework.

2. PRODUCT QUALITY TESTING

A representative from each participating company explained the methods used in its control laboratory to analyze and characterize products before shipment. These methods are summarized in Table 1. Significant remarks made on each test are noted below.

Ewen (PCA) stressed the importance of having critical tests done by the same experienced analyst. Detailed lab procedures and training may require more attention to achieve greater reproducibility and accuracy. The human factor should be recognized as an important variable in achieving consistent data from across the industry.

More emphasis should be placed on characterization of "Good" product sampled at destination or from points through the distribution system, as well as on diagnostic analyses on "Bad" or problem product. We continue to require a base of data on material which behaves well during storage, handling and transportation.

TESTS FOR COMPLIANCE WITH CANPOTEX SPECIFICATIONS

Composition: All companies use analyses which are checked against standards. Wet chemical or dry x-ray fluorescence techniques are used.

Particle Size Analysis: Standard screens are used to segregate dry product into size fractions which are weighed. Data are reported manually or by computer record. Agglomeration of reagentized fines may affect results. The prototype PCS Mining automatic particle size analyzer will be ready for trials in mid-December.

Reagent Type and Loading: There was no general discussion of the effectiveness of different types of reagents, although most producers use variations on long-chain amine and hydrocarbon oil treatments for anticaking and dedusting respectively. Reagent analyses are not currently a part of Canpotex specs., although some customers are now specifying reagent loading for their products, presumably based on their history experience with Canpotex shipments.

PRODUCT DURABILITY TESTS

Degradation: After discussion it was agreed that the PCS Mining "Wist" test would be evaluated by each producer, and that a sample of unreagentized granular product from the Cory Division be used as reference material for test calibration. The laboratory procedure and back-up data were distributed to participants. The cost of fabricating and distributing test apparatus to labs which require units would be estimated by PCS Mining R&D.

Comments from PCS Mining Divisions that have used the controlled ball-mill type test indicated that results provided a significant and useful index of product durability. Questions were raised about impact versus abrasion degradation and whether this selected test was appropriate. Renwick (Allan Division) has determined the degradation of product within narrow screen size ranges to detect any correlation between particle size and durability.

The screens used to separate degraded product should be new, because old, worn or damaged screens can yield different results.

Each mine site using other degradation test procedures for plant control purposes should contribute correlations between their standard test and the Wist test results. Ewen (PCA) noted that a general correlation has been developed to compare results from their control labs in Saskatchewan and New Brunswick.

Adoption of this Wist test would enable producers to provide Canpotex with common degradation indices on products. We recognized that this procedure would not predict performance of product during distribution. Other correlations between downstream exposure conditions and product durability would have to be either contributed by participants or developed by the project.

Dust in Product: Several producers use variations on a dust entrainment test. Dust which is generated by degradation or handling is suspended in air by fluidization, tumbling in an air stream, or by free-fall dispersion. Tests in general were dependent on the skill of the analyst and gave values which could be compared with other data from the same test. Results could not be intercompared.

Dust was found to be an environmental problem at transfer points (eg. rail to ship at Vancouver) and perhaps of concern to customers (dusty product must be poor product), however the participants did not agree that round-robin evaluation of a dusting test was required.

PCA has recorded dust entrainment for actual shipments using video equipment. Cominco has improved the uniformity of addition of dedusting oils to product at loadout by adjusting spray nozzle distribution.

TESTS FOR FREE-FLOWABILITY OF PRODUCT

Amine Loading: Typically amine and oils on product were extracted with an organic solvent and amines were then analyzed by colorimetric or other methods. An apparent decrease of detectable levels of amine with time (after addition to product) was noted by Renwick (Allan Division). Possible analytical interferences by minor or trace constituents of the product (e.g. iron) was noted by several participants.

Amine analyses are generally used to indicate if product will not cake. Experience has shown that if anticaking reagent is present at less than a threshold level, then product will tend to cake in storage.

Anticaking Tests: Control laboratories have done a great deal of work on development of reliable caking tests. These typically involve the storage of samples of product in forms, or as compressed material, in either the variable lab environment or in cabinets with humidity and temperature control. Experience with tests of these types has been mixed. There is difficulty in simulating actual field exposure conditions in the lab. Mayor (IMC) noted that they prefer field observations of product loaded with different levels of reagents to determine effective addition levels.

A major question in any procedure is the validity of materials samples used in the test. This, in turn, is dependent on the uniformity of coverage of the product with anticaking reagent. Where lab tests (eg. fracture of compressed pellets) are used, results are not reproducible and only trends in data collected under carefully repeated trials are found useful.

Experience of mill operators has yielded empirical correlations between caking properties and plant operating conditions. For example CCP, IMC, Kalium and Rocanville mills have found that the maximum drier temperature for crystallizer product inversely correlates with caking tendency (that is, high T, low caking). This phenomenon is attributed to incomplete removal of occluded moisture in crystallized product. Slow release of internally retained moisture from surface- dried material promotes caking in storage.

Care is required when humidity cabinets are used in the lab to simulate exposure conditions. It is important to confirm that stored product is equilibrated with the humidity-controlled air, as mass transport of moisture is slow. Cormode (Cominco) noted that field observations of product stored in railcars has shown that the apparent hygroscopicity of product can lead to absorption of moisture from air through closed ports.

There is scope for better defining the interaction between stored product and moisture in the air. Granular (vs standard sized) materials are more sensitive to moisture fluctuations.

There was general agreement that hard, dense compactor flake yielded the best granular product. Any porosity of granular material apparently facilitates moisture interaction and product degradation through capillary condensation cycles.

Ewen (PCA) noted that fines can contribute to product set-up, especially when vibratory compaction of product and in-filling of inter-granular voids is possible.

Moisture Measurements: These are done gravimetrically by weight loss at oven temperatures up to 110°C, or by extraction and Karl Fischer-type titration of removed H_2O.

Experience has shown that typical shipments are extremely low in detectable moisture (less than 0.1%) and correlations with downstream caking characteristics is poor. There is dissatisfaction with analyses of field sample moisture levels because moisture levels can change in handling the potash materials.

A more rapid method for field analyses of moisture levels is highly desirable and the project should consider this need.

3. FIELD EVALUATION OF PRODUCT PERFORMANCE

PCS Mining will consider this topic further and issue a revised technical proposal on field evaluation of potash materials. Participating producers will consider what specific data they require from the field to help diagnose the problem with deteriorated product.

Presently, production experts travel to inspect materials in storage or in their distribution system to evaluate problems. Samples are collected and analyzed in control labs to provide data on amine, moisture, size distribution, etc.

Little is known quantitatively about moisture changes within masses of granular potash materials, or about changes in temperature distributions in railcars, storage bins, piles, or ships. Studies of stacked materials in humidity controlled chambers need better instrumentation and monitoring.

The project leader will consult with companies again on the subjects of availability of specialized equipment for access by the project, on results and experience that has been achieved to date on field monitoring of products, and on recommendations for specific monitoring experiments.

4. REAGENTS FOR PRODUCT TREATMENT

Further consultation with individual producers is required to acquire recommendations on new reagent approaches and to learn about existing studies on reagent effectiveness. If necessary, a confidentiality agreement will be signed between PCS Mining and participating companies to ensure that proprietary information is limited to the offshore product quality project.

Results already reported on contact angle measurements between reagents and potash surfaces were reviewed by Strathdee (PCS Mining). This approach will be used to investigate anticaking reagent performance further.

Canpotex should acquire samples of offshore competitors' products so that we can identify the treatment reagents used by other suppliers.

Hrynewich (CCP) suggested that alternative inorganic anticaking reagents which have been found useful for other applications might also be evaluated as part of this project.

The project leader requested that participating companies compile or summarize existing internal information on the effectiveness of different reagents for product treatment. If necessary, a secrecy agreement will be signed. In addition, or alternatively, companies should provide the project leader with recommendations on reagent classes which should be evaluated during the term of the project.

NEXT MEETING

Any future meetings of participants will be arranged if and when required.

Graeme Strathdee,
November 26, 1986.

PARTICIPANTS IN OFFSHORE PRODUCT QUALITY PROJECT

MEETING NO.1, 1986.11.25

Name	Company	Title	Tel. No.
Graeme Strathdee	PCS Mining	Director R&D	933-8819
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Bill Wist	PCS Mining	Chief Chemist R&D	933-8835
Jim Mitchell	PCS Mining	Plant Supt.	257-3312
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Sylvia Wyton	PCS Mining Lanigan	Lab Supervisor	365-2030
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John Mayor	IMC	Chief Metallurgist	745-3931
Bruce Karras	PCS Sales	Director, Market Research	933-8694
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Don Irvine	PCS Mining	V.P. Engineering	933-8613
Garth Maki	PCS Ming.Rocanville	Mill Supt.	645-2870
Al Hickie	PCS Ming.Rocanville	Chief Metallurgist	645-2870
Doug Renwick	PCS Allan	Chief Metallurgist	257-3312
Irwin Ewen	PCA	Mill Superintendent	374-4800
Alex Cormode	Cominco	Supt. Eng. & Tech. Dev.	668-4343
Ross Mireau	Cominco	Analytical Super.	668-4343

APPENDIX IV

REPORT SUBMITTED TO THE

OFFSHORE PRODUCT QUALITY PROJECT

BY COMINCO LIMITED

FILE NOTE:

SUBJECT: RELATIONSHIP BETWEEN ABRASION RESISTANCE AND MOISTURE LEVEL

SUMMARY AND RECOMMENDATIONS

The effect of moisture on abrasion resistance of compacted potash products can be demonstrated by doing abrasion tests on samples as received and after drying. Quantifying the results to determine an exact relationship between abrasion resistance and moisture level has proven to be difficult. One of the observations has been that moisture distribution is non-uniform. Large particles were observed to have less moisture than smaller ones.

Results are presented in Tables 1 and 2 for samples with field and laboratory exposure. There is significant difference in the critical moisture level between field samples (0.020 - 0.064 % H_2O) and lab samples (0.134 - 0.252 % H_2O). Both tests indicate the same trend, as moisture levels increase abrasion resistance decreases. The laboratory tests were done in a very accelerated manner with 24 hour exposure in the humidity chamber with humidity levels in excess of 90% followed by forced air drying with cool air. Time may not have been sufficient to achieve equilibrium distribution with the granules. Moisture analyses were conducted coulometrically on a Metrohm 652 coulometer (Methanol extraction method). Abrasion analyses - see attachment.

DETAILS

Some exceptions and inconsistencies have been found in correlating the effect of moisture on abrasion resistance of compacted products. It had been the previous practice to do the moisture on the total sample whereas the abrasion test was conducted on a specific size fraction of the sample, namely the + 14 mesh material. This size fraction, as a percentage of the total sample can vary from 98% in classified material to 60% in severely degraded products.

It is generally assumed that a sample would, in terms of moisture content, come to equilibrium in a stable environment, either within a pile or a sealed sample bag. A detailed moisture test on a sample of wet coarse product (F-7) suggested that although the moisture content of a sample may in fact be in equilibrium, the large variance in surface area between product and fines results in a significant difference in the actual % H_2O content between product and fines.

SAMPLE	SIZE FRACTION	WT %	% H_2O
F-7	+ 14 Mesh	70	0.191
	- 14 Mesh	30	0.998
	Total	100	0.437

FILE NOTE:

SUBJECT: RELATIONSHIP BETWEEN ABRASION RESISTANCE AND MOISTURE LEVEL - Cont'd

DETAILS

A further series of moisture determinations were completed on a set of samples that were duplicates of the ones on which the abrasion tests were conducted. These results, listed in Table 1 - Field Samples, show that samples F-3 and F-5 actually had low moisture contents thereby explaining the good abrasion reistance of the material. The test also confirmed high moisture content in samples F-4, F-6 and F-7 which had low abrasion resistances. From this, it appears compacted products are able to easily withstand moisture levels of up to 0.02% H_2O (F-3), show severe degradation at a level of 0.064% H_2O (F-4) and complete breakdown at 0.952% H_2O (F-6). More testing will be done to verify these values and also to establish the actual critical moisture level our product can withstand. There are undoubtedly other factors such as the amount of fractures in compacted product which may give greater product degradation for the same moisture level compared to a better compacted product. This may well explain why some samples had severe degradation even at a modest moisture content.

As a compliment to the above tests, the development department conducted a lab test on production granular. A number of 300 gram samples of granular product (without the minus 14 mesh fraction) were placed in a humidity cabinet (see photo) and exposed to approximately 95% relative humidity for 24 hours. The samples were then dried in a forced air oven for 3 hours at 20°C. The samples were then assayed for abrasion resistance and moisture content. The variation in moisture levels in the samples arises from the unevenness of the air flow patterns in the humidity cabinet. The results are presented in Table 2.

TABLE 1 EFFECT OF MOISTURE CONTENT ON ABRASION RESISTANCE OF COMPACTED PRODUCTS FROM FIELD EXPOSURE

FIELD SAMPLES	ABRASION AS IS	ABRASION DRY	% H_2O TOTAL SAMPLE	% H_2O ABRASION SAMPLE
F1	96.4	95.7	0.026	0.014
F2	95.3	95.8	0.013	0.018
F3	96.6	97.5	0.062	0.020
F4	92.5	95.3	0.213	0.064
F5	96.3	97.9	0.221	0.015
F6	78.5	98.1	1.50	0.952
F7	93.0	97.8	0.437	0.191
F8	98.6	98.0	0.023	0.002

TABLE 2 EFFECT OF MOISTURE CONTENT ON ABRASION RESISTANCE OF COMPACTED GRANULAR FROM LAB EXPOSURE

LAB SAMPLES	ABRASION AS IS	% H_2O ABRASION SAMPLE
L1	98.1	0.042
L2	98.5	0.053
L3	98.0	0.058
L4	97.9	0.066
L5	97.7	0.081
L6	97.0	0.124
L7	97.2	0.134
L8	94.8	0.252
L9	92.4	0.327
L10	92.3	0.389
L11	88.8	0.509
L12	89.1	0.566
L13	83.2	0.780
L14	80.3	0.783

ABRASION RESISTANCE

SUMMARY

The estimation of a products abrasion resistance is achieved by shaking a specific size fraction of material with 450 grams of steel balls for ten minutes on a 20 mesh screen. The amount of material retained on the 20 mesh screen is weighed and reported as the percent abrasion resistance. This test works reasonably well as a control for plant production of compacted granular product, yielding a typical value of 97%. Inconsistencies in the method can occur when natural floated crystals are present, size distributions are radically different and significant moisture is present in the sample.

APPARATUS

Tyler Ro-Tap sieve shaker.
Tyler series sieves - 4 mesh, 14 mesh, 20 mesh and pan.
Balance, top loading 1/10 gram accuracy.
Steel balls, 450 grams of 1/2" dia. stainless steel.

PROCEDURE

Riffle out approximately 110 grams of sample. Assemble a sieve stack of 4 mesh, 14 mesh and a pan. Place the sample on 4 mesh sieve and shake for four minutes on Ro-Tap. Retain the -4 mesh +14 mesh fraction of the sample. Assemble a sieve stack with a pan below a 20 mesh sieve containing 450 grams of steel balls, add 100.0 grams of the -4 mesh +14 mesh product to the 20 mesh sieve and balls, cover and place in Ro-Tap with the hammer down. After shaking for 10 minutes weigh the abrasion resistant material by pouring the contents of the 20 mesh screen into a 1/4" screen held over the balance pan. Report this material, to the nearest 0.1 gram as the % Abrasion Resistance.

R.M. Mireau
Nov. 24, 1986

APPENDIX V

SELECTED REFERENCE MATERIAL

塩化ナトリウム粉体の水蒸気吸着と二，三の関連現象*

海保　守**　近沢正敏**　金沢孝文***

LIBRARY
-MINING-

Adsorption of Water Vapor on Sodium Chloride Powder and Several Related Phenomena

by

Mamoru KAIHO, Masatoshi CHIKAZAWA and Takafumi KANAZAWA

(Faculty of Technology, Tokyo Metropolitan University, Tokyo)

The effect of pre-adsorbed water on profiles of adsorption isotherms of water vapor on NaCl powder was investigated. Measurements were also made on volume shrinkage of the powder bed and surface area change of the particles during the water adsorption. And an interrelationship among the above three properties was discussed.

Each of the adsorption isotherms obtained showed a stepped increase in the amount of water adsorbed at the vapor pressure where the formation of two molecular layers completed. When the samples were heat-treated at above 200°C or ground in a dry atmosphere, the ratio of the step-width to monolayer capacity in the isotherms decreased. But when the samples were exposed to the repeated cycles of adsorbing ca. two layers of water followed by outgassing at room temperature, the above ratio was restored to the value for the untreated salt. When the amount of water adsorbed exceeded three layers, the powder particles began to aggregate and the surface area decreased.

(Received Feb. 24, 1973)

1　緒　　言

水溶性無機塩粒子上の吸着水層の厚みが増すと，微結晶やエッジのような不安定状態にある部分より溶解が始まる，と推定される．また吸着水層を介して，あるいは吸着水の脱離に際して，溶解した塩が析出してくることも予想される．吸湿固結の初期過程と関連して重要な意味を持つこれらの現象は，従来ほとんど解明されていない．

水溶性無機塩の例として NaCl を採りあげ，再結晶法および摩砕によって得た同粉体について，水蒸気吸着前後の水蒸気吸着等温線[1)-3)]，比表面積[2)]，粉体層の収縮，などの変化を求め，相互の関連性を検討した．

2　実 験 方 法

試料には2種類の粉体 Nr, Ng を使用した．Nr は NaCl 特級試薬の熱飽和水溶液を冷却したエチルアルコール上にスプレーで吹きかけ，生成した沈殿を沪別後，乾燥して得た．Ng は NaCl 特級試薬を乾燥ふん囲気中においてメノウ乳鉢で摩砕して 200 メッシュを全通させて得た．検鏡によれば，Nr の大部分は一辺 1～4μ 程度の立方体の結晶であり，一部には他の形状（林状など）に成長したものも認められた．また Ng は特に規則性の外形を持たない粒子からなり，粒径も一定していないものであった．比表面積は両者とも 0.3 m²/g 程度であった．

水蒸気吸着量の測定は既報[1)]に準ずる．比表面積は窒素を用いた BET 法で測定した．容積収縮は粉体層の上に立てた指示針の示す高さの変化をカセトメータで読み取って求めた．

3　結果と考察

3・1　再結晶試料の吸着等温線と吸着熱

Fig. 1 の Nr の水蒸気吸着等温線は，B 点を基準とした場合に，2分子層を完成する付近から階段状の立ち上がり（step）を示した．その後，圧上昇につれて吸着量もゆるやかに増加していき，約6分子層形成後，CRH（飽和水溶液の平衡水蒸気圧）に近づくにつれ吸着量が急激に増加した．Step は吸着層がより密な状態へと構造変化するため生じる，と一般に解釈されている．また CRH 近くでの立ち上がりは，吸着層がバルクな液体へと変化することに対応するものであろう．

Fig. 1 から各温度における平衡圧を求め，Clausius-Clapeyron 式に代入すると，Fig. 2 の等量吸着熱変化

* 原稿受理　昭和48年2月24日
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無機塩類の接触角の測定

大川原　武*・門　田　稔*

On the Measurements of Contact Angle of Inorganic Salts

Takeshi OKAWARA and Minoru KADOTA

Abstract

To measure the contact angle which the liquid forms when it drops on the solid matter has been known to be one of the simplest methods to show to what extent the solid matter becomes wet by using the liquid.

We intend to try to apply the aforementioned method measuring the contact angle, to the measurement of the inorganic salt in order to know the floatability of the inorganic salt using the changes of the contact angles. For this purpose, we carried out the measurement of the contact angle between the one including sodium chloride, potassium chloride, calcium sulfate, and the other including each salty saturated solution added by surface active agent.

The results thus obtained are shown as below:

1) The contact angle of saturated solution against sodium chloride was 21.5°–23.0°. And the contact angle in the case of the saturated solution of sodium chloride including sodium oleate was 13.0°–14.0°, while its surface active agent concentration was 100–125 mg/l.

2) The contact angle of saturated solution against potassium chloride was 19.5°–20.5°. The contact angle in the case of the saturated solution of potassium chloride including sodium laurylsulfate was 14.0°–15.3°, while its surface active agent concentration was 10 mg/l.

The contact angle of the saturated solution against potassium chloride when it was added sodium oleate, was 29.5°–30.5°, on the other hand, its surface active agent concentration was 175–200 mg/l.

3) In connection with the contact angle between calcium sulfate and its saturated solution, it was 15.5°–16.5°. The contact angle of saturated solution of calcium sulfate which was added sodium laurylsulfate, was 11.0°–13.0° with the surface active agent concentration of 50 mg/l.

In the end, the contact angle of the saturated solution of calcium sulfate which was added sodium oleate, was 13.5°–15.5° with the surface active agent concentration of 25–30 mg/l.

Judging from the results of these experiments, we can testify that the use of sodium oleate is required as colector for the purpose of the flotation of sodium chloride, and that the use of sodium laurylsulfate is required for the purpose of the flotation of potassium chloride.

1. 緒　　言

浮遊選鉱法は今日種々の鉱石や石炭などの品位を上げる手段として広く応用されてお

* Department of Applied Chemistry.

TABLE 6. COMPARISON OF CONTACT ANGLES ON KCl AND NaCl

Reagent	Surface Tension dyn/cm	Contact angle on KCL at R.H. of 0% ° ± 1°	45% ° ± 1°	90% ° ± 1°	Contact angle on NaCl at R.H. of 0% ° ± 1°	45% ° ± 1°	90% ° ± 1°
decane	42.1	0	0	0	0	0	0
decyl amine	28.4	15	34	24	15	30	23
heptanoic acid	15.5	8	9	5	8	9	6
heptyl alcohol	27.9	15	19	15	15	20	15
heptyl amine	26.4	17	22	14	17	17	15
nonyl alcohol	28.6	24	32	27	24	34	28
octyl amine	27.0	10	15	11	10	16	10